VOL.
2
1956

Journal of
Inorganic & Nuclear Chemistry

VOLUME II

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PERGAMON PRESS · LONDON · NEW YORK 1956

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PERGAMON PRESS, INC., 122 E. 55TH STREET, NEW YORK 22, N.Y.

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J. Inorganic and Nuclear Chemistry, 1956, Vol. 2, pp. 1–10. Pergamon Press Ltd., London

ON THE STABILITIES OF TRANSITION METAL COMPLEXES—I

THEORY OF THE ENERGIES

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(*Received* 14 *July* 1955)

Abstract—A molecular orbital theory of the energies of formation of transition metal complexes is presented. The energies of pairing of *d*-electrons in covalent regular octahedral d^n-complexes are calculated in terms of atomic spectral parameters. It is then shown, by means of a hole formalism, that the pairing energies for regular tetrahedral d^{10-n}-complexes are formally the same. A reason is suggested as to why regular complexes with certain spins, which are apparently possible in principle, are unknown experimentally. Certain aspects of the electrostatic crystal-field theory are briefly compared with the present treatment.

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1. INTRODUCTION

AMONGST the complexes of transition series elements two kinds have been distinguished on the basis of their magnetic properties. In the first the total spin of the complex is the same as that of the constituent metal ion in its ground state in the gas phase. These have been called by PAULING[1] "ionic" or "essentially ionic" complexes. In the second the *d*-electrons are crowded as far as possible into those *d*-orbitals which cannot be used to form σ-bonds with the ligands. For elements in the middle of the transition series this means that the total spin is one or two units less than the spin of the corresponding essentially ionic complex. PAULING called these "covalent" or "essentially covalent" complexes. TAUBE[2] has suggested calling the two kinds outer and inner orbital complexes respectively. As in these papers we find no compelling reason for preferring the new notation, we use that of PAULING.

There are two main methods of theoretical treatment of these complexes—BETHE's of the electrostatic crystal field and MULLIKEN's of molecular orbitals. These, and also PAULING's method of the directed bond, were compared by VAN VLECK[3] and shown to lead to broadly the same conclusions. The complexes concerned had a high degree of symmetry, and the conclusions depended more upon the nature of the symmetry group than upon the detailed assumptions of the theories. The electrostatic field model has been used by VAN VLECK and his co-workers[4, 5, 6] to explain the magnetic susceptibilities, and also later by other workers to interpret paramagnetic resonance absorption measurements (for review, see BLEANEY & STEVENS[7]).

*Now at the Department of Theoretical Chemistry, University of Cambridge.

[1] PAULING, L. (1940) *The Nature of the Chemical Bond*, p. 115. Oxford University Press.
[2] TAUBE, H. (1952) *Chem. Rev.*, **50**, 85.
[3] VAN VLECK, J. H. (1935) *J. Chem. Phys.*, **3**, 807.
[4] SCHLAPP, R., and PENNEY, W. G. (1932) *Phys. Rev.*, **42**, 666.
[5] JORDAHL, O. M. (1934) *Phys. Rev.*, **45**, 87.
[6] HOWARD, J. B. (1935) *J. Chem. Phys.*, **3**, 813.
[7] BLEANEY, B., and STEVENS, K. W. H. (1953) *Rep. Progr. Phys.*, **16**, 108.

The optical spectrum of a complex was first interpreted in detail by FINKELSTEIN and VAN VLECK.[8] For other spectra, see for example, OWEN.[9]

The general reasons for the quenching of the spin in covalent complexes are clear enough,[3] but detailed calculations do not appear to have been published. In the first paper of this series, a theoretical discussion of the quenching is presented. It is impracticable to solve the complete wave equation for the complex, and so any treatment must be approximate. We shall be interested mainly in the energies of the

TABLE 1.—CHARACTER TABLE OF THE SYMMETRY GROUPS O AND T_d

	E	$8C_3$	$3C_2$	$6(C_2;\ \sigma_d)$	$6(C_4;\ S_4)$
A_1	1	1	1	1	1
A_2	1	1	1	−1	−1
E	2	−1	2	0	0
T_1	3	0	−1	−1	1
T_2	3	0	−1	1	−1

complexes and regard them as built up from two parts—the central metal ion and its ligands. Then we shall neglect π-bonding, and discuss the energy of the d-shell of the ion in terms of the normal theory of the spectra of many-electron atoms without configuration interaction. In fact we assume Russell-Saunders coupling and leave the spin-orbit coupling out of the Hamiltonian. This omission seems a reasonable first approximation for the first transition series; however, for the second and third series the spin-orbit coupling is larger, whilst the intra-atomic electronic repulsions are smaller, and so it may not even be a useful first approximation there. The interaction of the metal ion with its ligands is treated by means of an averaged field molecular orbital theory, and, at present, we consider only regular octahedral and regular tetrahedral complexes.

These assumptions are of course very restrictive; nevertheless it is felt that none of the essential physical features of the quenching of the spin have been omitted. There is, however, a consequent gain of generality which makes it possible to discuss all the complexes at once and not as a set of independent cases. This is partly due to the fact that the rotation group of a regular octahedron is simply isomorphic with the full symmetry group of a regular tetrahedron. Further, the five d functions on the metal form, for both groups, a representation which is the direct sum of two irreducible representations which have the dimensions 2 and 3 (see Tables 1 and 2).

2. THE BONDING IN THE COMPLEXES

We suppose the energy of a complex to consist of two distinct parts—that of bonding of the ligands and that, if any, needed to pair the d-electrons in quenching the spin. We treat the bonding first, by means of an averaged field molecular orbital theory with inclusion of nearest-neighbour overlap. For this we use the simplest possible model, taking only one valence orbital on each ligand, and considering only the σ-overlap and resonance integrals of these orbitals with the metal valence orbitals. These ligand

[8] FINKELSTEIN, R., and VAN VLECK, J. H. (1940) *J. Chem. Phys.*, **8**, 790.
[9] OWEN, J. (1955) *Proc. Roy. Soc.*, **A227**, 183.

orbitals may be regarded as lone-pair hybrids, typical examples being the lone pairs of H_2O or NH_3. We then consider the behaviour of these orbitals under the operations of the octahedral group O (without inversion) and the tetrahedral group T_d (with

TABLE 2.—THE REPRESENTATIONS SPANNED BY THE ATOMIC ORBITALS. SMALL LETTERS ARE USED FOR REPRESENTATIONS HAVING ONE-ELECTRON FUNCTIONS AS A BASIS

	Octahedral	Tetrahedral
Metal s	a_1	a_1
Metal p	t_1	t_2
Metal d	$e + t_2$	$e + t_2$
Ligand lone pairs	$a_1 + e + t_1$	$a_1 + t_2$

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reflections). These groups are both simply isomorphic with the symmetric group on four symbols, and have the character table shown in Table 1. The behaviour of the orbitals on the central metal ion is shown in Table 2. There are four lone-pair orbitals in the tetrahedral and six in the octahedral case. They form reducible representations whose irreducible components are also shown in Table 2.

We consider specifically the first transition-series ions, where the valence shell consists of $3d$, $4s$, and $4p$, with $4d$ and higher atomic orbitals of less importance. If we include the $4d$, many of the molecular orbitals (symmetry orbitals) of the system have to be determined as a combination of an orbital on the ligand molecules with several orbitals on the central atom. Thus, in the tetrahedral case, a lone-pair symmetry orbital belonging to t_2 can combine with $3d$, $4p$, and $4d$ on the metal. For this reason we consider first the general problem of the solution of the secular equations for a particular irreducible representation, for the interaction of one ligand orbital with several metal orbitals.

We take ϕ_0 on the ligands belonging to a particular irreducible representation X, say. Then each set of metal orbitals which forms a basis for X can be arranged to have just one orbital with a non-zero overlap with ϕ_0. We neglect the possibility of accidental degeneracy, and arrange these metal orbitals in order of increasing energy, writing them $\phi_1, \phi_2, \cdots, \phi_n$.

The secular equations are

$$f(E) \equiv |H_{ij} - ES_{ij}| = 0,$$

where $$H_{ii} < H_{jj} \text{ for } i < j \text{ and } i, j = 1, 2, \cdots, n. \tag{1}$$

In discussing (1), we take the metal orbitals orthonormal and also with their mutual resonance integrals zero. This is automatically true for those belonging to different representations of the three-dimensional rotation group, and is a natural requirement in general. Then $|H_{ij} - ES_{ij}|$ has zero elements except for its first row and column and its main diagonal, and can easily be expanded, giving

$$f(E) \equiv \prod_{i=0}^{n} (H_{ii} - E) - \sum_{i=1}^{n} (H_{oi} - ES_{oi})^2 \prod_{j \neq o,i} (H_{jj} - E). \tag{2}$$

From (2) we have

$$f(H_{oo}) = -\sum_{i=1}^{n} (H_{oi} - H_{oo}S_{oi})^2 \prod_{j\neq o,i} (H_{jj} - H_{oo}),$$

$$f(H_{ii}) = -(H_{oi} - H_{ii}S_{oi})^2 \prod_{j\neq o,i} (H_{jj} - H_{ii})$$

$$(i = 1, \cdots, n). \tag{3}$$

We assume that none of the $(H_{oi} - H_{ii}S_{oi})$ are zero and then find, from (1) and (3), that $f(H_{ii})$ has the same sign as $(-1)^i$. For $|E|$ large:

$$f(E) = (-E)^{n+1}(1 - \sum_{i=1}^{n} S_{oi}^2) + O(|E|^n). \tag{4}$$

In (4) $\sum S_{oi}^2$ is never as large as 1, so $f(-\infty) = +\infty$. Also, for E large and positive, $f(E)$ has the same sign as $(-1)^{n+1}$. This means that the roots of $f(E) = 0$ are separated by $-\infty$, H_{ii} and $+\infty$. These findings are summed up in equation (5):

$$E_o < H_{11} < E_1 < \cdots H_{ii} < E_i < \cdots H_{nn} < E_n. \tag{5}$$

It is natural to suppose that $H_{oo} < H_{ii}$ for all $i \neq 0$, otherwise there would be too great a transfer of charge to the metal. We assume this, and can then deduce from (3) that

$$E_o < H_{oo} < H_{11} < E_1 . \tag{6}$$

Writing $\psi_i(X)$ for a molecular orbital of symmetry X corresponding to E_i in (5), the orbitals of lowest energy in the complex are the $\psi_o(X)$. There are the same number of these as there are ligands, and so the electrons initially in the lone-pair orbitals will go into these. This leaves in the valence shell only the 3*d*-electrons from the metal to be housed. We shall say that $\psi_i(X)$ corresponds to an atomic orbital $\phi_i(X)$ if their energies are related in the sense of E_i and H_{ii} in (5). If ϕ_i does not interact with ligand orbitals, then $\psi_i(X) \equiv \phi_i(X)$. Since, in the free ion, the 3*d*-orbitals lie lowest, we suppose that the 3*d*-electrons are housed in $\psi_1(e)$ and $\psi_1(t_2)$. We write Δ for the difference of energy between these representations, and λ for the number of electrons in the upper one. If Δ is small, HUND's rule will apply to the whole *d*-shell and the complex will be ionic. If Δ is large, the electrons will crowd into the lower level with a consequent gain of orbital energy. However, there will be additional coulomb repulsions and a loss of exchange energy. Then the energy of the complex may be written

$$E = p + P + \lambda\Delta, \tag{7}$$

where p represents the part of the energy which is not very sensitive to the value of λ—that is: the solvation energy of the whole complex; mutual interactions between the ligands; and the orbital energy of the ψ_o. P represents any energy required to pair *d*-electrons in the lower representation ψ_1. This lower representation consists of pure 3*d*-orbitals, and in the next section we evaluate P from the theory of atomic spectra.

Before doing this we discuss briefly in terms of (7) the meanings of the ground states of the various kinds of complex. For the ionic complex, P is zero whilst λ is as small as possible consistent with the complex having the same spin as the corresponding free ion. These values of λ are shown in Table 8 for octahedral complexes. In section 1 we also defined covalent complexes, and again λ has the minimum value

consistent with the total spin. PAULING[1] pointed out that there is in principle a third class of complex possible. For octahedral complexes the spin of d^5- and d^6-ions could be quenched by only one unit, leaving spins of 3/2 and 1 respectively. A similar thing is possible for d^4 and d^5 tetrahedral complexes. We shall call these half-quenched complexes. The spins and electron arrangements for octahedral symmetry are shown in Table 3. In comparing stabilities we suppose p to be the same for the three types of the same complex.

TABLE 3.—THE THREE TYPES OF REGULAR OCTAHEDRAL COMPLEXES

(*a*) *Total spin*

	Ionic	Half-quenched	Covalent
d^4	2	—	1
d^5	$2\frac{1}{2}$	$1\frac{1}{2}$	$\frac{1}{2}$
d^6	2	1	0
d^7	$1\frac{1}{2}$	—	$\frac{1}{2}$

(*b*) *Arrangements of electrons for a d^6 complex.*

	t_2	e	Example
Ionic	↑↓ ↑ ↑	↑ ↑	$Fe^{++}(H_2O)_6$
Half-quenched	↑↓ ↑↓ ↑	↑ ○	unknown
Covalent	↑↓ ↑↓ ↑↓	○ ○	$Fe(CN)_6^{4-}$

3. CALCULATION OF THE PAIRING ENERGY

We regard the calculation of the pairing energy P as a purely atomic problem closely analogous to the determination of the energy of a valence state relative to an atomic ground state. Thus, although the electrons are paired in directions away from those of the bonds, we do not consider any other effects of the ligands, for these have already been taken into account in the terms p and $\lambda\Delta$ in (7).

We take axes $OXYZ$ with O at the metal nucleus. The octahedral bonds are taken along these axes, and the tetrahedral bonds along the vectors (1, 1, 1), (1, −1, −1), (−1, 1, −1), (−1, −1, 1). Then, introducing atomic orbitals $|nlm\rangle$ quantized with respect to the Z-axis, we are interested only in the 3d-orbitals and write

$$|m\rangle = |32m\rangle, \tag{8}$$

where the orbitals $|m\rangle$ are connected by the Dirac phase relation and with $|O\rangle$ real. Then $|1\rangle$, $|-1\rangle$ and $(1/\sqrt{2})(|2\rangle + |-2\rangle) \in t_2$ and $|O\rangle$ and $(1/\sqrt{2})(|2\rangle - |-2\rangle) \in e$,

for both types of complex. It is convenient to use real orbitals, and so we write

$$\begin{aligned}
|\xi\rangle &= -(1/\sqrt{-2})(|1\rangle + |-1\rangle),\\
|\eta\rangle &= -(1/\sqrt{2})(|1\rangle - |-1\rangle),\\
|\zeta\rangle &= (1/\sqrt{-2})(|2\rangle - |-2\rangle),\\
|\epsilon\rangle &= (1/\sqrt{2})(|2\rangle + |-2\rangle),
\end{aligned} \tag{9}$$

and have $(|\xi\rangle, |\eta\rangle, |\zeta\rangle) \in t_2$ and $(|O\rangle, |\epsilon\rangle) \in e$. In equation (9), $|\xi\rangle$, $|\eta\rangle$, $|\zeta\rangle$, and $|\epsilon\rangle$ are identical save for spatial orientation. We shall express P in terms of RACAH's parameters A, B, and C, these being related to the Slater-Condon F_i by the equations[10]

$$\begin{aligned}
A &= F_0 - 49F_4,\\
B &= F_2 - 5F_4,\\
C &= 35F_4.
\end{aligned} \tag{10}$$

Coulomb and exchange integrals are normally defined in terms of the $|m\rangle$, but for our complexes it is much more convenient to work in terms of $|\xi\rangle$, $|\eta\rangle$, $|\zeta\rangle$, $|\epsilon\rangle$, and $|O\rangle$. The exchange integrals J and K, where

$$\begin{aligned}
J(ab) &= \langle ab|V|ab\rangle,\\
K(ab) &= \langle ab|V|ba\rangle,
\end{aligned} \tag{11}$$

may be evaluated in terms of A, B, and C, the results being shown in Table 4. With the use of these we now calculate the energies of the ground states. These are well known

TABLE 4.—COULOMB AND EXCHANGE INTEGRALS WITHIN A d-SHELL

Orbital pair	J	K
$\xi\xi, \eta\eta, \zeta\zeta, \epsilon\epsilon, OO$	$A + 4B + 3C$	$A + 4B + 3C$
$\xi\eta, \eta\zeta, \zeta\xi, \xi\epsilon, \eta\epsilon$	$A - 2B + C$	$3B + C$
$\xi O, \eta O$	$A + 2B + C$	$B + C$
$\zeta O, \epsilon O$	$A - 4B + C$	$4B + C$
$\epsilon\zeta$	$A + 4B + C$	C

for the ions, the first column of Table 6 being taken from CATALAN, ROHRLICH, and SHENSTONE[11]. The other cases are calculated assuming a strong field, which means that for covalent complexes the electrons in a d^n-ion are in a configuration $t_2^n (n \leqslant 6)$ and $t_2^6 e^{n-6} (n > 6)$ in the octahedral, and $e^n (n \leqslant 4)$ and $e^4 t_2^{n-4} (n > 4)$ in the tetrahedral case. We shall see that a strong field is needed to quench the spin, so this seems a reasonable approximation. In Table 5, the symmetries of the lowest states are shown. It is seen that the covalent states all form irreducible representations and their energies can therefore be calculated immediately, but that the half-quenched

[10] RACAH, G., (1942) *Phys. Rev.* **62**, 452.
[11] CATALAN, M. A., ROHRLICH, F., and SHENSTONE, A. G. (1954) *Proc. Roy. Soc.*, **A221**, 421.

TABLE 5.—SYMMETRIES OF GROUND STATES OF COMPLEXES

Tetrahedral	Octahedral	Ionic	Half-quenched	Covalent
d^8	d^4	E	—	T_1
d^5	d^5	A_1	$T_1 + T_2$	T_2
d^4	d^6	T_2	$T_1 + T_2$	A_1
d^3	d^7	T_1	—	E

states form reducible representations. The expression for the energy of a covalent ion is thus the familiar one

$$E = \sum_{k<1} J(k, 1) - \sum_{k<1} K(k, 1), \tag{12}$$

where the exchange integral $K(k, 1)$ is zero for pairs $(k, 1)$ with differing spin. The results of the calculations for the covalent states are also shown in Table 6.

TABLE 6.—ENERGIES OF GROUND STATES OF IONS

	Ionic	Octahedral		Tetrahedral	
		Half-quenched	Covalent	Half-quenched	Covalent
d^3	$3A - 15B$	—	—	—	$3A - 8B + 4C$
d^4	$6A - 21B$	—	$6A - 15B + 5C$	$6A - 16B + 5C$	$6A - 16B + 8C$
d^5	$10A - 35B$	$10A - 25B + 6C$	$10A - 20B + 10C$	$10A - 25B + 6C$	$10A - 20B + 10C$
d^6	$15A - 35B + 7C$	$15A - 30B + 12C$	$15A - 30B + 15C$	—	$15A - 29B + 12C$
d^7	$21A - 43B + 14C$	—	$21A - 36B + 18C$	—	—

This leaves the half-quenched states, and we illustrate the evaluation of the energies of the ground configurations of these in detail only for the octahedral d^5-ion. The total spin of the ground configuration is 3/2, and we take $S_z = 3/2$, giving as basic states

$$\begin{aligned} \psi_1 &= |\xi\alpha\xi\beta\eta\alpha\zeta\alpha O\alpha\rangle, & \psi_4 &= |\xi\alpha\xi\beta\eta\alpha\zeta\alpha\epsilon\alpha\rangle, \\ \psi_2 &= |\xi\alpha\eta\alpha\eta\beta\zeta\alpha O\alpha\rangle, & \psi_5 &= |\xi\alpha\eta\alpha\eta\beta\zeta\alpha\epsilon\alpha\rangle, \\ \psi_3 &= |\xi\alpha\eta\alpha\zeta\alpha\zeta\beta O\alpha\rangle, & \psi_6 &= |\xi\alpha\eta\alpha\zeta\alpha\zeta\beta\epsilon\alpha\rangle. \end{aligned} \tag{13}$$

Writing $V_{ij} = \langle\bar{\psi}_i|V|\psi_j\rangle$ for the matrix of the electrostatic energy, we find

$$\begin{aligned} V_{11} = V_{22} &= 10A - 19B + 6C, \\ V_{33} &= 10A - 25B + 6C, \\ V_{44} = V_{55} &= 10A - 23B + 6C, \\ V_{66} &= 10A - 17B + 6C. \end{aligned} \tag{14}$$

Knowing that the ψ_i between them span $T_1 + T_2$, it is unnecessary to evaluate any off-diagonal V_{ij}. Both ψ_3 and ψ_6 have a special relationship to the Z-axis. Calling ψ'_3, ψ'_6 and ψ''_3, ψ''_6 the corresponding functions having exactly the same relationship to the X- and Y-axes respectively, it is easy to verify that all the operations of O

transform $(\psi_3, \psi'_3, \psi''_3)$ amongst themselves, and also $(\psi_6, \psi'_6, \psi''_6)$ amongst themselves. In fact

$$\begin{aligned}(\psi_3, \psi'_3, \psi''_3) &\in T_1,\\ (\psi_6, \psi'_6, \psi''_6) &\in T_2,\end{aligned} \tag{15}$$

and so the energies are given by

$$\begin{aligned}E(T_1) &= V_{33} = 10A - 25B + 6C,\\ E(T_2) &= V_{66} = 10A - 17B + 6C.\end{aligned} \tag{16}$$

In a similar way the energies of the half-quenched d^6 octahedral ion are

$$\begin{aligned}E(T_1) &= 15A - 30B + 12C,\\ E(T_2) &= 15A - 22B + 12C.\end{aligned} \tag{17}$$

The energies of the various ground configurations of tetrahedral complexes could be calculated in the same way. This, however, is unnecessary, for we may deduce them from the energies for the octahedral case by a method due, in essence, to SHORTLEY[12], who showed that the matrix of electrostatic energy for a shell which was complete except for ϵ "missing" electrons was simply related to the matrix for the same shell containing just ϵ-electrons. We need only diagonal elements of the electrostatic energy, and correlate a state $\psi(O) = |d_1, \ldots, d_\epsilon\rangle$ for the octahedral with $\psi(T_d) = |d_{\epsilon+1}, \ldots, d_{10}\rangle$ for the tetrahedral case. If $\psi(O)$ belongs to the ground configuration for an octahedral ion of a given kind, then it is clear that $\psi(T_d)$ belongs to the ground configuration of a tetrahedral ion of the same kind (i.e., also ionic, half-quenched, or covalent). By considering the behaviour of the missing electrons from a wave function of the tetrahedral kind, it is clear that symmetry is conserved under the correlation. Thus, for example, the states of the ground configuration of a covalent d^4 octahedral complex are correlated with the states of the ground configuration of a covalent d^6 tetrahedral complex, and both have the symmetry T_1. Writing $V(O)$ and $V(T_d)$ for the electrostatic energies, we have:[12, 13]

$$\begin{aligned}V(T_d) &= V(d^{10}) - \sum_{i=1}^{10}\sum_{j=1}^{\epsilon}(J(d_i d_j) - K(d_i d_j)) + V(O)\\ &= 45A - 70B + 35C - \epsilon(9A - 14B + 7C) + V(O).\end{aligned} \tag{18}$$

Here ϵ is the number of electrons missing from the d-shell of the tetrahedral ion. In (18) the first two terms depend only upon ϵ, and not upon whether the complex is ionic, half-quenched, or covalent. This means that the pairing energies for a d^ϵ tetrahedral ion are formally the same as those for a $d^{10-\epsilon}$-octahedral ion. These results are illustrated in Tables 5, 6, and 7. Table 5 shows the symmetries and Table 6 the energies of the ground states, whilst Table 7 gives the mean pairing energies defined in the next section.

[12] CONDON, E. U., and SHORTLEY, G. H. (1953) *The Theory of Atomic Spectra*, pp. 284, 295. Cambridge University Press.
[13] CONDON and SHORTLEY, 1953, p. 296.

4. THE NON-EXISTENCE OF REGULAR COMPLEXES WITH HALF-QUENCHED SPINS

It is seen from Table 3 that, as the spin of the ionic state is quenched by μ units, the value of λ also decreases by μ units, so from equation (7) the increase of energy of the complex is

$$\delta E = P - \mu\Delta\,. \tag{19}$$

Hence the reaction involving the quenching of the spin is exothermic if

$$\Delta > \mu^{-1}P\,. \tag{20}$$

It is therefore convenient to give $\mu^{-1}P$ a symbol and a name. We write it Π and call it the mean pairing energy. It is the same as P except for the octahedral covalent d^5 and d^6 and the tetrahedral covalent d^4 and d^5 complexes. The calculated values of Π are shown in Table 7.

TABLE 7.—MEAN PAIRING ENERGIES $\Pi(n)$

Tetrahedral	Octahedral	Half-quenched	Covalent
d^6	d^4	—	$6B + 5C$
d^5	d^5	$10B + 6C$	$7\frac{1}{2}B + 5C$
d^4	d^6	$5B + 5C$	$2\frac{1}{2}B + 4C$
d^3	d^7	—	$7B + 4C$

Now, in order to decide which of the three possible forms of a complex should be found experimentally, we must consider the free-energy changes involved in the reactions

$$(MA_n)_i \rightleftharpoons (MA_n)_h \rightleftharpoons (MA_n)_c. \tag{21}$$

In (21) we let ΔF_i, ΔF_h, and ΔF_c be the standard free energies of formation of the three species, with a corresponding notation for the heat contents H and the entropies S. Then

$$\begin{aligned}\Delta F_h - \tfrac{1}{2}(\Delta F_i + \Delta F_c) &= \Delta H_h - \tfrac{1}{2}(\Delta H_i + \Delta H_c) - T(\Delta S_h - \tfrac{1}{2}(\Delta S_i + \Delta S_c)) \\ &= 2\tfrac{1}{2}B + C - T(\Delta S_h - \tfrac{1}{2}(\Delta S_i + \Delta S_c)),\end{aligned} \tag{22}$$

from Table 7 in all four of the relevant cases. From atomic spectral data[11] $2\frac{1}{2}B + C$ is of the order of 20 kilocalories, whilst it is improbable that $T(\Delta S_h - \frac{1}{2}(\Delta S_i + \Delta S_c))$ is more than 2–3 kilocalories. This means that, whatever the value of Δ, either the ionic or the covalent complex has a considerably lower free energy than the corresponding half-quenched one. Accordingly, it appears that half-quenched spins are impossible for complexes with regular octahedral or tetrahedral symmetry. They are unknown experimentally for these symmetries. This conclusion is unlikely to be altered by a consideration of π-bonding or by small distortions such as would be expected for orbitally degenerate complexes. However, half-quenched spins are certainly possible in principle for complexes with a lower symmetry, such as certain haemoglobin complexes,[14] although it is improbable that they occur in fact.[15]

[11] GRIFFITH, J. S., (1955) Faraday Soc. Discussion on Microwave and Radio-frequency Spectroscopy, to be published.
[15] GRIFFITH, J. S., to be published.

5. RELATIONSHIP TO THE ELECTROSTATIC THEORY.

By taking $P = 0$ in equation (7), we have a formula for the energy of an ionic complex which appears to be rather different from that which would be obtained from an electrostatic field theory. The origin of the difference is that, in an electrostatic

TABLE 8.—λ AND THE EXTRA STABILIZATION $(\lambda - 2n/5)$ FOR IONIC COMPLEXES

Complex	λ	$\lambda - 2n/5$
d^0	0	0
d^1	0	−2/5
d^2	0	−4/5
d^3	0	−6/5
d^4	1	−3/5
d^5	2	0
d^6	2	−2/5
d^7	2	−4/5
d^8	2	−6/5
d^9	3	−3/5
d^{10}	4	0

theory, the mean orbital energy of the d-shell is unchanged by the field, whilst in a molecular orbital theory it is raised. By shifting it, we can bring the two theories into coincidence. This is shown in equation (20),

$$E = (p + 2n\Delta/5) + (\lambda - 2n/5)\Delta, \tag{20}$$

where $(p + 2n\Delta/5)$ still changes uniformly with n, but $(\lambda - 2n/5)\Delta$ gives just the extra stabilization given by an electrostatic theory. The values of λ and $\lambda - 2n/5$ are shown in Table 8. This comparison has been given for the strong-field case for which the additional stabilization for d^2 and d^7 is $-4\Delta/5$, but can easily be extended to cover the weak-field case in which this stabilization is $-3\Delta/5$.

The reason that the two theories give the same results is, fundamentally, that they both predict that the d-shell is split into the two parts, e and t_2, determined by the symmetry groups. So the discussions in Sections 3 and 4 would be virtually unaltered with an electrostatic theory. However, the physical origin of the splitting appears to be quite different in the two cases, and the theories should be regarded more as supplementary than alternative. We may expect the electrostatic effect to be large in K_3FeF_6, but the molecular orbital splitting to be predominant in $K_3Fe(CN)_6$. Yet there will be both types of splitting in both compounds. There is, however, a difference between the theories, because with the electrostatic theory there is, to a first order in perturbation, no charge transfer to the ligands. This transfer is a natural consequence of any molecular orbital theory, and has been used by STEVENS[16] in interpreting paramagnetic resonance measurements.

The author is indebted to Dr. P. GEORGE for his comments on the manuscript.

[16] STEVENS, K. W. H. (1953) *Proc. Roy. Soc.*, **A219**, 542.

J. Inorganic and Nuclear Chemistry, 1956, Vol. 2, pp. 11–31. Pergamon Press Ltd., London

INFLUENCE OF FLUORINE SUBSTITUTION ON THE PROPERTIES OF METAL CHELATE COMPOUNDS—I

COPPER(II) CHELATES OF BIDENTATE LIGANDS[1]

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(*Received* 20 *June* 1955)

Abstract—The ultraviolet, visible, and infrared absorption spectra of six β-diketones and their copper(II) chelates are presented and discussed in relation to the structure of these molecules. Infrared assignments are made. The 300-mμ bands of the metal chelates are shown to be shifted enolate ion absorptions. The order of magnitude and direction of those shifts are predicted correctly by a simple molecular orbital-electrostatic calculation. Visible chelate spectra are correlated with the nature of the chelating agent. The correlation agrees with crystal-field theory predictions. Preparations of most substances studied are described in full, as are some problems arising from the preparations.

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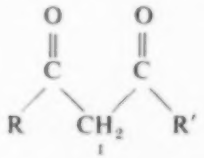
THIS is the first of three articles dealing with the influence of fluorine substitution in the ligand on the properties of metal chelate compounds. Although the primary purpose of this project was to study the influence of fluorine substitution on the properties—particularly light absorption—of uranyl compounds, copper chelates were chosen for preliminary study as model substances, because they are easily prepared. Since a number of fluorinated bidentate ligands are available or may be readily prepared, it was decided to investigate copper(II) chelates of these substances first. The ligands selected for this study are represented by Formula I, and the corresponding metal chelate compounds by Formula II. The names and structures of the metal chelate compounds prepared are given in Table 1 by defining the substituent groups R and R′ in each case.



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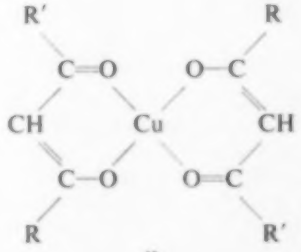

II

Although bis-acetylacetono-Cu(II) was first studied early in the development of co-ordination chemistry,[4, 5, 6] the fluoro-derivatives of acetylacetone and similar ligands have not been available until recently, and relatively little has been done

[1] The work described in this paper was sponsored by the U.S. Atomic Energy Commission.
[2] National Science Foundation Predoctoral Fellow, 1953–4 and 1954–5.
[3] On leave during summer of 1953 from Clark University, Worcester, Massachusetts.
[4] A. COMBES, *Compt. rend.*, **105**, 868 (1887).
[5] L. CLAISEN and E. EHRHARDT, *Ber.*, **22**, 1009 (1889).
[6] H. LEY, *Ber.*, **47**, 2948 (1915).

TABLE 1.—BIDENTATE LIGANDS AND CU(II) CHELATES

Name of Ligand	Formula*		References†	
	R	R′	Ligand	Cu(II) Chelate
Acetylacetone	CH_3	CH_3	—	4, 5, 6
Trifluoroacetylacetone	CF_3	CH_3	7, 8	8, 9, 10
Hexafluoroacetylacetone	CF_3	CF_3	10	10
Ethylacetoacetate	CH_3	OC_2H_5	12	9, 12
Ethyltrifluoroacetoacetate	CF_3	OC_2H_5	—	9, 10
Acetoacetic acid diethylamide	CH_3	$N(C_2H_5)_2$	11	11

* R and R′ refer to the corresponding groups in Formulas I and II.
† Reference numbers refer to footnotes in main body of paper.

with the corresponding metal chelates. Trifluoroacetylacetone has been studied by a number of investigators.[7, 8] Although the stability of *bis*-(trifluoroacetylacetono)-Cu(II) was reported in 1945,[9] the first reports of the preparation of the compound appeared somewhat later.[7, 8] Some reactions of hexafluoroacetylacetone have been studied by HASZELDINE *et al.*[10]

Of the remaining substances listed in Table 1, the diethylamide of acetoacetic acid and its copper(II) chelate have been investigated by UTZINGER.[11] Also, the stability of the copper chelate of ethylacetoacetate has been reported by CALVIN and WILSON,[9] and an absorption maximum in the ultraviolet has been reported by MORTON and RASNEY.[12]

EXPERIMENTAL

Bis-(Trifluoroacetylacetono)-Cu(II)

To 10·0 g (0·050 mole) of cupric acetate monohydrate dissolved in 150 ml of warm water was added a solution of 15·4 g (0·010 mole) of trifluoroacetylacetone in 25 ml of ethanol. The reaction mixture was warmed and stirred, 1·2 g of anhydrous sodium carbonate were added, and the heating was continued for fifteen minutes more. The blue precipitate which had first appeared when the solutions were mixed was filtered off and recrystallized from 50 per cent aqueous ethanol. The hot solution was green, but turned greenish-blue on cooling, and a robin's-egg-blue alcoholate crystallized out. The product was filtered and air-dried, whereupon it became blue-lavender in appearance. The final yield was 17·1 g, or 92 per cent of the theoretical amount. The compound was found to be soluble in cold chloroform, toluene, and benzene, to give blue solutions, and is very soluble in hot chloroform, toluene, and benzene, to give green solutions. It is not readily recovered from these solutions by cooling, but it may be recrystallized easily by cooling a hot carbon tetrachloride solution.

[7] A. HENNE, M. NEWMAN, L. QUILL and R. STANIFORTH, *J. Amer. Chem. Soc.*, **69**, 1819 (1947).
[8] J. C. REID and M. CALVIN, *J. Amer. Chem. Soc.*, **72**, 2948 (1950).
[9] M. CALVIN and K. WILSON, *J. Amer. Chem. Soc.*, **67**, 2005 (1945).
[10] R. N. HASZELDINE, W. K. MUSGRAVE, F. SMITH, and L. M. TURTON, *J. Chem. Soc.*, 609 (1951).
[11] G. E. UTZINGER, *Helv. Chim. Acta*, **35**, 1359 (1952).
[12] R. MORTON and W. RASNEY, *J. Chem. Soc.*, 707 (1926).

It sublimes readily, a relatively large sample having been obtained in one hour at 100° and 0·1-mm pressure. An attempt to determine the melting-point resulted in slow sublimation above 140°C. The melting-point obtained is 189°, in agreement with that reported by REID and CALVIN[8] and by PARK *et al.*[13]

Anal. Calcd. for $C_{10}H_6O_4F_6Cu$: C 32·5, H 2·2. Found: C 32·3, H 2·5.

Hexafluoroacetylacetone

A 50-g sample (approximately 0·20 mole) of hexafluoroacetylacetone dihydrate, obtained from the Caribou Chemical Company, was shaken with approximately three times its volume of 98 per cent sulphuric acid until the material was completely dispersed. The heat evolved during the initial stages of dehydration was removed by immersion of the flask in cold water for a short time. After the mixture had been allowed to stand overnight, the anhydrous hexafluoroacetylacetone was seen to separate as a colourless liquid over the sulphuric acid, which was deeply coloured by decomposed organic material. Dehydration of the product was repeated with a fresh batch of sulphuric acid. The final product was siphoned off and distilled. It was found that about 98 per cent of the liquid distilled between 70·0 and 70·2°C. Qualitative observation indicated that the liquid has a low viscosity, low surface tension, high vapour pressure, and that it hydrates rapidly when exposed to the atmosphere. Its density, measured by weighing the liquid delivered from a 0·02-ml micro-pipette, was found to be 1·46 g/ml.

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Anal. Calcd. for $C_5H_2O_2F_6$: C 28·82, H 0·97. Found: C 28·81, H 1·13.

Acidic hydrogen: Calcd. mol. wt: 208. Found: 205.

Bis-(Hexafluoroacetylacetono)-Cu(II) (Method I)

To 10·0 g (0·05 mole) of cupric acetate dissolved in 150 ml of water, 25 g (0·1 mole) of hexafluoroacetylacetone dihydrate were added with stirring. The solution turned green, and pale green crystals gradually appeared. Upon the slow addition of 25 ml of 4·0 *M* sodium hydroxide, the solution deepened in colour and the amount of crystalline precipitate increased. After the reaction mixture was heated on a steam bath for an hour, it was cooled, and the product was filtered off. When it was recrystallized from 50 per cent ethanol, a greenish-yellow solvate, consisting of long, flat, radiating needles, was obtained. When stood in air, the solvate decomposed and the needles crumbled, forming a green finely-divided solid. The product weighed 14·0 g, or 55 per cent of the theoretical amount, calculated as the dihydrate. It was found to be insoluble in water, but soluble in ethanol, dioxane, and organic solvents containing polar groups. It sublimed readily onto a cold finger in a drying pistol heated by boiling chloroform, a moderate-sized sample being collected in five hours. Its melting-point was found to be 135°.

Anal. Calcd. for $C_{10}H_2O_4F_{12}Cu \cdot 2H_2O$: C 23·4, H 1·17. Found: C 23·16, H 1·16.

(*Method II*).—A 2·0-g sample of cupric acetate monohydrate was dissolved in 10 ml of anhydrous hexafluoroacetylacetone by boiling for five minutes. The excess reagent was evaporated off, and the residue was recrystallized from carbon tetrachloride. The yield of the resulting grass-green crystalline product weighed 4·5 g, or 80 per cent of the theoretical amount.

Bis-Ethylacetoacetato-Cu(II)

To 10 g (0·05 mole) of cupric acetate dissolved in 100 ml of hot 50 per cent aqueous ethanol were added 13 g (0·1 mole) of ethylacetoacetate dissolved in 25 ml of ethanol. The mixture was heated on a steam bath until most of the alcohol had been expelled, and was cooled. The green-blue powder obtained upon filtration and air-drying was likely a hydrate. It was recrystallized twice successively from hot ligroin-chloroform mixture, the first time yielding a bluish powder, the second, large green plates. They melt at 193°C, with decomposition.

Anal. Calcd. for $C_{12}H_{18}O_6Cu$: C 44·8, H 5·64, Cu 19·8. Found: C 44·94, H 5·78, Cu 19·9.

Bis-(Ethyltrifluoroacetoacetato)-Cu(II)

To a solution of 2·0 g (0·010 mole) copper(II) acetate monohydrate in 100 ml of dioxane were added 3·68 g (0·02 mole) of ethyltrifluoroacetoacetate. The blue colour of the copper acetate was quickly

[13] J. D. PARK, H. A. BROWN and J. R. LACHER, *J. Amer. Chem. Soc.*, **75**, 4754 (1953).

changed to deep green. The reaction mixture was warmed for fifteen minutes with 1·0 g of potassium carbonate, the excess base was filtered off, and the solution was diluted with an equal volume of water. After the light green crystalline product which separated was filtered, washed, and air-dried, it was found to weigh 3·7 g, which corresponds to 86 per cent of the theoretical yield. This product was recrystallized from 150 ml of carbon tetrachloride; it was obtained in the form of deep green crystals. It was found to be very soluble in acetone, chloroform, and dioxane, but insoluble in ligroin and water. Its melting point was 188°.

Anal. Calcd. for $C_{12}H_{12}O_6F_6Cu$: C 33·5, H 2·8, Cu 14·8. Found: C 31·2, H 2·9, Cu 15·0.

Reaction of diethylamine with ethyltrifluoroacetoacetate

To 50 ml of anhydrous diethylamine were added, dropwise with stirring, 15 g (0·08 mole) of ethyltrifluoroacetoacetate. To the reaction mixture was added 100 ml *i*-octane, and the solution was reduced to 20 per cent of its original volume by low-pressure distillation. Upon cooling to 0°C, it yielded 12 g of white crystals. They were washed with ice-cold *i*-pentane, recrystallized from *i*-octane, and dried *in vacuo*. The product is soluble in all organic solvents tried—from saturated hydrocarbons to ketones and alcohols—at room temperature. Its melting-point is 82°.

Anal. Calcd. for $C_8H_{12}NO_2F_3$(N,N-diethyltrifluoroacetoacetamide): C 45·5, H 5·69, N 6·64. Calcd. for $C_{10}H_{16}NO_2F_3$(β-diethylamino ethyltrifluorocrotonate): C 50·0, H 6·76, N 5·84. Found: C 51·7, H, 6·97, N 5·55.

Basic groups: Calcd. for $CF_3C[N(C_2H_5)_2]CHCO_2C_2H_5$: 1 basic amino group/239 g. Found: 1 basic group/238 g.

Reaction of β-diethylamino ethyltrifluorocrotonate with Cu(II)

To 21·1 g (0.10 mole) of the above product dissolved in 100 ml of warm absolute ethanol were added 10 g (0·05 mole) of cupric acetate monohydrate. The metal salt gradually dissolved when the reaction mixture was boiled for ten minutes, and a deep green solution was formed. After the solution had been cooled and diluted with an equal volume of water, a deep green crystalline precipitate was isolated. The weight of product obtained was 21 g, or 86 per cent of the theoretical yield, based on the expected copper(II) chelate. The product was recrystallized from a small amount of chloroform by adding *n*-heptane. After further recrystallization from carbon tetrachloride, it was obtained in the form of deep greenish-blue crystals, very soluble in chloroform, acetone, and alcohols, sparingly soluble in carbon tetrachloride and in ligroin, and nearly insoluble in cold *n*-heptane.

Anal. Found: N 0·0, Cu 15·1.

Titrations

All titration curves were measured with a glass electrode in conjunction with a Beckman pH meter. Frequent checks vs. standard buffer solutions were made.

Hexafluoroacetylacetone was pipetted and the weight calculated from the measured density 1·46 g/ml). It was titrated with 0·100 *N* NaOH.

One sample of β-diethylamino ethyltrifluorocrotonate was titrated with 0·385 *N* HCl. The resulting solution, at pH 1·9, was allowed to stand on a steam bath for two hours. A titration with 0·83 *N* KOH showed that no reaction had occurred in the hot acidic solution.

Absorption spectra

The infrared absorption spectra were measured with a Model 21 Perkin-Elmer Recording Double-Beam Spectrophotometer with NaCl optics. The liquid ligands were measured as thin films, while the solid ligands, hexafluoroacetylacetone dihydrate and β-diethylamino ethyltrifluorocrotonate, as well as all of the metal chelate compounds, were measured in the form of nujol mulls. Frequencies are estimated accurate to 10 cm^{-1}.

Some of the absorption spectra in the visible and ultraviolet were measured with a Cary Model 11 recording spectrophotometer; the others in the near infrared, visible and ultraviolet, were measured with a prototype of the Beckman DK Recording Spectrophotometer at fast speed in the ultraviolet, medium speed in the visible and infrared. Quartz cells of 1-cm thickness were employed. The solutions were first made up by weight to 0·01 *M*, and these solutions were then successively diluted by

syringe-type pipettes until absorption of the sample could be accurately measured. With few exceptions, the spectroscopic solvent employed was Eastman Kodak No. S337 Spectro Grade chloroform. Sodium-dried B & A reagent-grade ether, distilled water, Phillips spectro-grade cyclohexane and absolute methanol were used in the special cases.

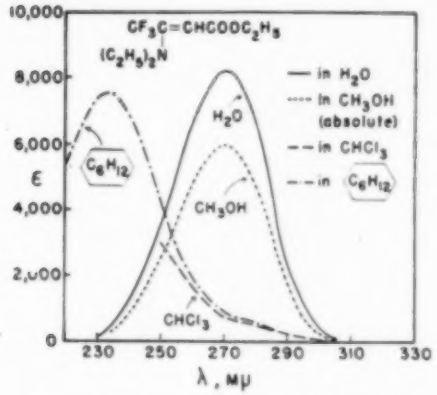

FIG. 1.—Ultraviolet spectra of β-diethylamino ethyltrifluorocrotonate, 10^{-4} *M* in water, methanol, chloroform and cyclohexane.

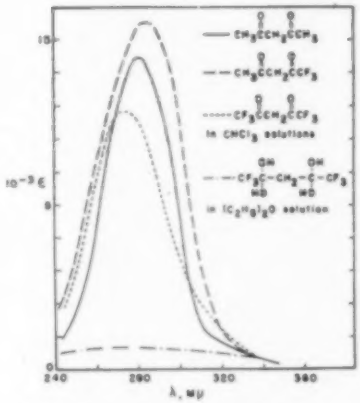

FIG. 2.—Ultraviolet absorption spectra of acetylacetone, ——, trifluoroacetylacetone, – – –; and hexafluoroacetylacetone, – – – –; $4{\cdot}0 \times 10^{-5}$ *M* in $CHCl_3$; of hexafluoroacetylacetone dihydrate, $4{\cdot}0 \times 10^{-5}$ *M* in ether.

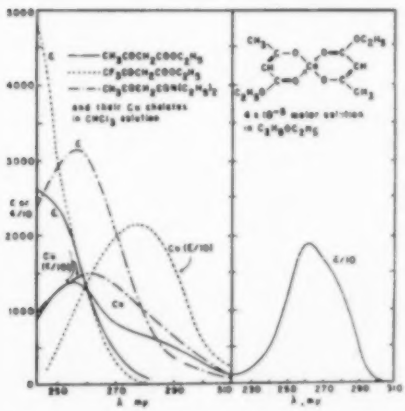

FIG. 3.—Ultraviolet absorption spectra of (left): ethylacetoacetate,——; ethyltrifluoroacetoacetate, – – –; and N,N-diethylacetoacetamide, — · —. 2×10^{-4} *M* in $CHCl_3$. The corresponding Cu chelates, 2×10^{-5} *M* or 1×10^{-5} *M* in $CHCl_3$, are labelled "Cu". (right): *bis*-ethylacetoacetato-Ca(II), 4×10^{-5} *M* in absolute ether.

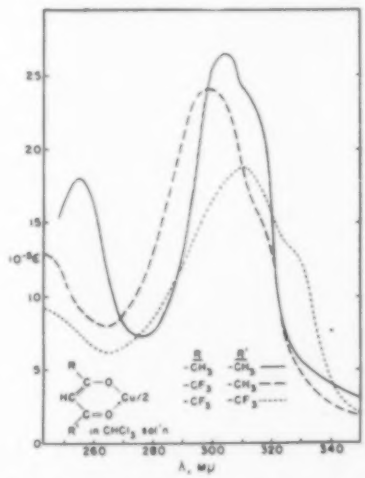

FIG. 4.—Ultraviolet absorption spectra of 2×10^{-5} *M* *bis*-acetylacetono-Cu(II), ——; 2×10^{-5} *M* *bis*-trifluoroacetylacetono-Cu(II), – – – –; and 1×10^{-5} *M* *bis*-hexafluoroacetylacetono-Cu(II), – – –; in $CHCl_3$.

EXPERIMENTAL RESULTS

Fig. 1 shows the ultraviolet absorption spectra of β-diethylamino ethyltrifluorocrotonate in a variety of solvents. The ultraviolet absorption spectra of the ligands are given in Figs. 2 and 3, and the corresponding spectra of the copper(II) chelate compounds are given in Figs. 3 and 4. Figs. 5 and 6 illustrate the visible

absorption spectra of the six copper(II) chelate compounds reported in this investigation. In each case molar extinction coefficient, based on the presumed formula weight, is plotted vs. wavelength in mμ. The wavelengths of the maximum of the

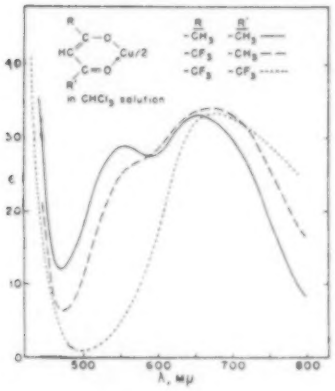

FIG. 5.—Visible absorption spectra of *bis*-acetylacetono-Cu(II), ——; *bis*-trifluoroacetylacetono-Cu(II), — — —; and *bis*-hexafluoroacetylacetono-Cu(II), – – –; 0·010 *M* in $CHCl_3$.

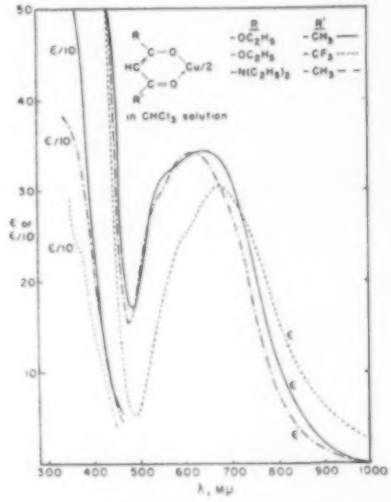

FIG. 6.—Visible absorption spectra of *bis*-ethylacetoacetato-Cu(II), ——; *bis*-ethyltrifluoroacetoacetato-Cu(II), – – –; and *bis*-N,N-diethylacetoacetamido-Cu(II), — · —; 0·010 *M* in $CHCl_3$. Left-hand curves obtained with 0·0010 *M* solutions.

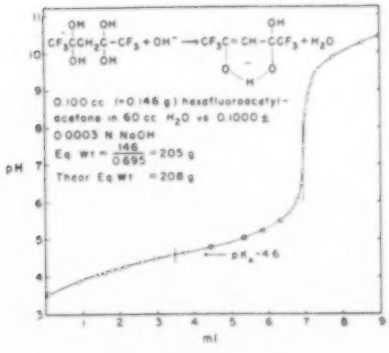

FIG. 7.—Titration of aqueous hexafluoroacetylacetone with sodium hydroxide solution.

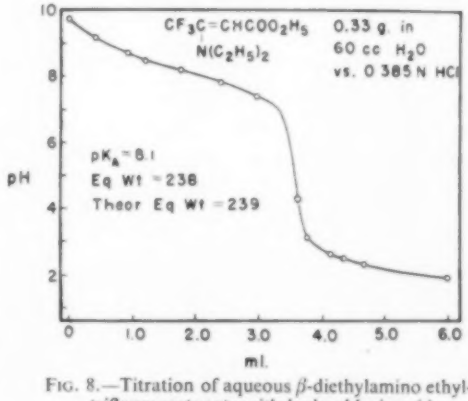

FIG. 8.—Titration of aqueous β-diethylamino ethyltrifluorocrotonate with hydrochloric acid.

absorption bands found in the visible and ultraviolet regions of the spectrum are listed in Table 2, along with the corresponding approximate molar extinction coefficients. In certain cases the irregular shape of a shoulder of the absorption band indicated probable additional bands adjacent to and partly obscured by the primary band. Such subsidiary bands are indicated in parentheses in Table 2, when it was possible to estimate approximate frequencies.

TABLE 2.—ABSORPTION BANDS OF $CHCl_3$ SOLUTIONS IN THE VISIBLE AND ULTRAVIOLET REGIONS

Compound	Molarity	λ_{max}	ε_{max}
I Acetylacetone	4×10^{-5}	280	9,500
II Trifluoroacetylacetone	4×10^{-5}	284	10,500
III Hexafluoroacetylacetone dihydrate*	4×10^{-5}	none	—
IIIa Hexafluoroacetylacetone	4×10^{-5}	273	7,800
IV Ethylacetoacetate	2×10^{-4}	<246	~2,600
V Ethyltrifluoroacetoacetate		<246 (~290)	~4,900
VI N,N-diethylacetoacetamide	2×10^{-4}	256 (Utzinger gives $\lambda_{max} = 253$, $\log \varepsilon = 4{\cdot}0$)*	3,200
I-Cu *bis*-acetylacetono-Cu(II)	2×10^{-5}	254 304 (313) (390)	18,000 26,000 — —
	1×10^{-2}	552 660	29 33
II-Cu *bis*-trifluoroacetylacetono-Cu(II)	2×10^{-5}	298 (316)	24,000 —
	1×10^{-2}	(566) 680	— 34
III-Cu *bis*-hexafluoroacetylacetono-Cu(II)	1×10^{-4}	310 (329)	18,700 —
	1×10^{-2}	710	40
IV-Cu *bis*-ethylacetoacetato-Cu(II)	2×10^{-5}	254 (281)	14,000 —
	1×10^{-2}	(560) 650	— 34
V-Cu *bis*-ethyltrifluoroacetoacetato-Cu(II)	2×10^{-5} 1×10^{-2}	277 (590) 680	22,000 30
VI-Cu *bis*-N,N-diethylacetoacetamido-Cu(II)	1×10^{-5} 1×10^{-2}	260 (540) 620	~16,000 — 34

* Dissolved in diethyl ether rather than $CHCl_3$.

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TABLE 3a.—INFRARED ABSORPTION BANDS OF BIDENTATE LIGANDS

Region	I	II	III	IIIa	IV	V	VI	VII*
OH str.	3550	3360 (3120)	3330	3120	3550	3360 (3100)	3480	((3500)) ((3100))
CH str.	2960 (2620) (2350)	2980 (2350)	(2500) (2330) (2160)	2950 (2580) 2420 (2200) 2000	3050	2920 2340	2960 (2350)	 ((2520)) ((2430))
C=O and C—C str.	(1725) 1708 1620	1775 1745 (1713) 1680		1790 1765 1680 1625	1735 1720 1650 (1640)	1650 1608 (1562) 1545	1720 1640 1595 (1560)	1688 1635 1560
		(1475)			1470	(1525) (1510) (1475)	(1545) 1495	(1545)
CH_3 and CH_2 de- form; C—C str.	 1425 1365 1305 1252	1455 (1430) 1375 1350 1282	 1340 1278	1450 (1350) 1270	1450 1410 1370 (1265)	(1460) 1425 1375 1285	1460 1390 1365 1315 1280	1495 1390 1335 1275
		1230 1200	1212	1220	1235	1207	1223	1190
	1175 (1162) (1025) 1003 957 918	1160 1095 1030 (990) 900	1188 1138 990 970 910	1160 1085 913	1190 1150 (1115) 1096 1037 (928)	1157 1112 (1030) (895)	1205 1142 1100 1080 1038 1010 963 943 920	1165 1130 1110 1098 (1065) 1030 963 913
		822	823	819	(855)	858	826	863 837
	780	730 700	740 720	743	(740)	795 726	790 775 725	790 725
		665	658	655	662		670	675

* β-diethylaminoethyltrifluorocrotonate.

The infrared absorption frequencies are listed in Table 3a for the ligands and in Table 3b for the corresponding metal chelate compounds. Here, also, frequencies of very weak or doubtful bands are enclosed in parentheses.

Titration curves are given in Figs. 7 and 8. From Figs. 7 and 8 we estimate the pK_A for hexafluoroacetylacetone to be about 4·6; for ethyltrifluorocrotonate β-diethylammonium ion, about 8·1.

TABLE 3b.—INFRARED ABSORPTON BANDS OF BIDENTATE Cu(II) CHELATES

I-Cu	II-Cu	III-Cu	IV-Cu	V-Cu	VI-Cu
(2360)	(2350)	(2350)	(2340)	(3110)	(2340)
1582	1615	1643	(1645)	1635	1565
(1560)	1535	(1615)	1600	1612	(1550)
1530		1565	1555	1564	1525
		1540	1538	(1550)	1500
		1490		1495	
(1425)	(1422)	(1450)	(1425)	(1432)	(1440)
(1362)	1312	1360	1250	1375	1398
1278	1230	(1340)	(1270)	1312	1363
1193	1198	(1300)	(1225)	1248	1343
	1157	1260	1180	1230	1302
	1142	1210		1228	(1280)
		1150		1188	1212
		1110		1155	1167
					1102
1020	1030	1080	1070	1092	1085
940	1015	1044	1022	1013	1075
(720)	952	(955)	985	985	1050
682	870	(895)	973	967	(1030)
	800	871	(865)	925	1000
	738	802	778	862	970
		746	(758)	842	960
		679		815	928
				802	830
				755	785
				732	728
				722	670
				698	

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DISCUSSION

Preparation of Ligands and Cu(II) Chelate Compounds

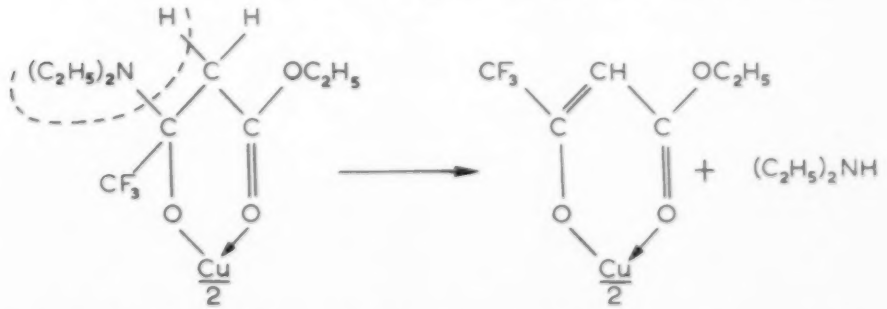
All of the ligands excepting N,N-diethylacetoacetamide, and β-diethylamino ethyltrifluorocrotonate, were available from commercial sources. The former compound, and its Cu(II) chelate, were kindly donated by Dr. G. E. UTZINGER.[11] The product obtained from the reaction of diethylamine with ethyltrifluoroacetoacetate always contained less nitrogen than that calculated for the desired product, N,N-diethyltrifluoroacetoacetamide, but corresponded quite closely to the value calculated for β-diethylamino ethyltrifluorocrotonate. This structure for the product was confirmed by titration curves, absorption spectra, and failure to obtain a nitrogen-containing copper chelate.

The method described for the preparation and purification of hexafluoroacetylacetone from the dihydrate has not been reported previously, and seems to be an

improvement over the method given by HASZELDINE *et al.*,[10] which involves the treatment of an ether solution of the hydrate with metallic sodium. The resulting solution was used for synthesis of other metal salts, rather than for the preparation of the pure diketone. The boiling-point range found in this investigation is quite narrow, and differs somewhat from the values reported by HASZELDINE *et al.*[10] (54–85°), and by HENNE *et al.*[7] (63–65°). The apparently impure fraction obtained by HASZELDINE and co-workers was obtained by treatment with sodium sulphate in ether, and probably was a partially dehydrated mixture.

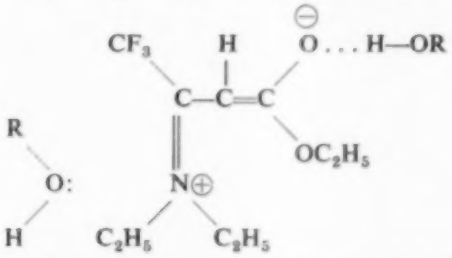
The procedures used for the preparation of the copper(II) chelates of trifluoroacetylacetone, ethylacetoacetate and of ethyltrifluoroacetoacetate, are sufficiently different from the procedures previously reported[7, 8, 10, 11,] to warrant the brief descriptions given here. The preparation of the copper(II) chelate compounds of trifluoroacetylacetone given above has not been described previously, although it has apparently been prepared by HENNE *et al.*[7] In the preparation of *bis*-hexafluoroacetylacetono-Cu(II) the results of the present investigation indicate that, contrary to the findings of HASZELDINE *et al.*,[10] the metal chelate is formed in the presence of water. On the other hand, there is general agreement in that the yield of metal chelate seems much higher in non-aqueous media.

The reaction of copper(II) acetate monohydrate with β-diethylaminoethyltrifluorocrotonate in boiling ethanol resulted in a product free of nitrogen. The analytical results checked the theoretical values of *bis*-ethyltrifluoroacetoacetato-Cu(II) and, with the exception of some rather minor differences, the infrared and ultraviolet spectra of the latter compound also corresponded very closely to those of the reaction product. It seems, therefore, that the diethylamino group was replaced by a hydroxy group. That this process of hydrolysis (or alcoholysis) must be metal-catalyzed is shown by the previously mentioned titration experiments; one should certainly observe hydrolysis products by titration, since the pK_A of the liberated diethylamine would be >11. However, prolonged heating of the free amino-crotonic ester in aqueous solutions ranging from neutral to quite acid yielded quantitatively the initial undecomposed amine, $pK_A \sim 8{\cdot}1$. A likely mechanism for metal-catalyzed hydrolysis would involve the hydrate either in the transition state or as stable intermediate:

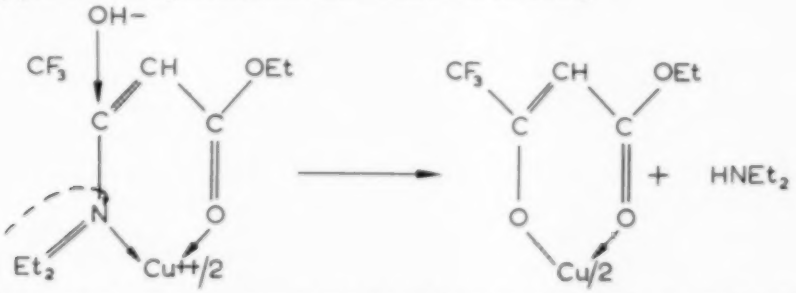


Accordingly, ultraviolet spectra of the crotonate (Fig. 1) were examined for that disappearance of high-intensity bands which would mark extensive conversion of the crotonate to a solvent (HOH or ROH) addition product across the double bond. No such evidence is to be seen; indeed, in the hydroxylated solvents not only is the principal band quite as strong as in cyclohexane or chloroform, but it has undergone

a shift from 234 to 270 mμ. This indicates that the hydroxylated solvents must assist excitation of the conjugated system, perhaps through such forms as



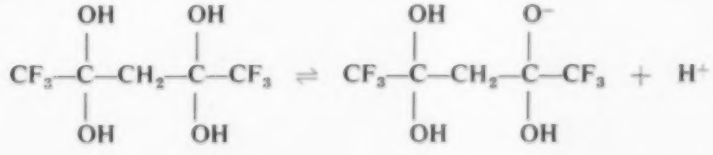
The question which this interpretation leaves unanswered is why chloroform, a hydrogen-bonding agent, does not exhibit a similar effect. Perhaps the steric hindrance would be sufficient to prevent useful approach of chloroform, or perhaps chloroform's H-bonding power is just not great enough to be observed here. Since there appears to be no positive evidence for large equilibrium quantities of $(C_2H_5)_2NC(CF_3)(OH)CH_2CO_2C_2H_5$ when the crotonate is dissolved in water or alcohol, the above elimination reaction may not involve such a species at all. Instead, it may proceed through some such mechanism as the following,



which invokes the polarizing power of the doubly-charged cation to weaken the C—N bond.

The low metal and carbon analyses of *bis*-hexafluoroacetylacetono-Cu(II), and a high hydrogen analysis indicate the possibility of a dihydrate, but this chelate compound sublimed very readily without change in colour or composition. Also, there were no hydroxyl bands in the infrared. Since it is unlikely that a hydrate of any kind could be produced without the retention of O—H bonds, the conclusion is inevitable that the analytical results are in error and that the chelate is anhydrous, with a structure corresponding to Formula I.

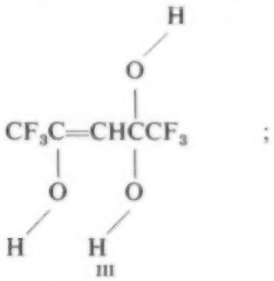
Another experience would indicate that hexafluoroacetylacetone anion is indeed no more than monohydrated. The titration with 0·100 *N* base (Fig.7) shows hexafluoroacetylacetone to be an acid slightly stronger than acetic acid. However. the equilibrium



would probably have a much higher pK_A; other known alcohols very highly substituted with trifluoromethyl groups have acid pK-values no smaller than about 10 (e.g., $(C_3F_7)_2CHOH$, $pK_A = 10{\cdot}66$; $(C_3F_7)_3COH$, $pK_A = 10{\cdot}1$.)[14] (One might conjecture that the four hydroxy-groups would increase the acidity of each other and of the methylene hydrogens. Likely this effect could not account for such great acidity as we observe, however. An inductive-effect calculation, with consideration of the statistical factor, sets a lower limit on the pK_A for the dihydrate of *ca.* 8.) The alternative reaction would seem to be one involving dehydration,

$$CF_3C(OH)_2CH_2C(OH)_2CF_3 + OH^- \rightleftharpoons CF_3C(OH){=}CH_2C(OH)_2CF_3 + H_2O$$

The pK_A value observed should then correspond to the acid structure



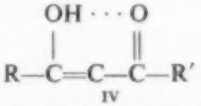
III

in fact, 4·6 would be a reasonable value for this enol.

MORGAN and MOSS[15] have pointed out that metal chelate compounds of Type II, in which two beta-diketonic residues are bound to a transition metal, form stable addition compounds with two other donors to give complexes in which the metal co-ordinate linkages are presumed to have an octahedral arrangement. In this investigation no addition compounds were obtained under the conditions employed in the production of *bis*-acetylacetono-Cu(II). However, this tendency was apparent in the case of *bis*-trifluoroacetylacetono-Cu(II), for which an unstable solvate formed in cold 50 per cent aqueous ethanol and gradually decomposed to the anhydrous form when exposed to air over the period of a few hours. It is perhaps surprising that more stable addition compounds were not obtained for the hexafluoroacetylacetone chelate, since the tendency of the trifluoromethyl groups to decrease stability[9] would be expected to enhance the affinity of the metal ion for additional donor groups. However, an unstable solvate, perhaps also an alcoholate, was first isolated when the chelate was recrystallized from aqueous ethanol. Samples of *bis*-hexafluoroacetylacetono-Cu(II) prepared from the dihydrate of the ligand in aqueous media, and from the diketonic form of the ligand in anhydrous media, both gave products with identical properties and spectra.

Ultraviolet and Visible Absorption Spectra

All of the ultraviolet absorption bands of ligands in Figs. 2 and 3 are high-intensity bands arising from electronic transitions in the conjugated system:

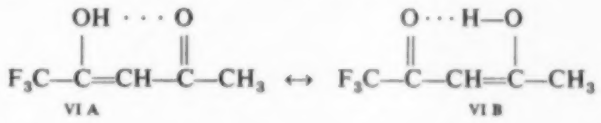


IV

[14] A. HENNE, *J. Amer. Chem. Soc.*, **75**, 991 (1953), and R. N. HASZELDINE, referred to therein.
[15] G. T. MORGAN and H. W. MOSS, *J. Chem. Soc.*, **105**, 189 (1914).

Such bands are sometimes called "K" transitions.[16] This enolic system, in which R may be methyl or trifluoromethyl, and R′ may be methyl, trifluoromethyl, ethoxy, or diethylamino, is common to all of the ligands investigated.

In Fig. 2, a simple comparison may be made between the spectra of acetylacetone and its trifluoro and hexafluoro derivatives. The maximum of the intense absorption band of acetylacetone is shifted to longer wavelengths and further intensified by the substitution of an electron-attracting trifluoromethyl group at one end of the conjugated system. In this case two isomeric enol forms are possible:



VI A VI B

The influence of the trifluoromethyl group increases enolization;[8] one may surely suppose that A has greater acidity than B, and therefore that B is likely present in higher concentration than A. The absorption band of hexafluoroacetylacetone, on the other hand, is considerably decreased in intensity, while its frequency is also decreased. A rough quantitative comparison of these spectra on the basis of relative intensities is possible, even though the relative degrees of enolization are not known exactly. From published data on the absorption intensity of the pure enol of acetylacetone, one would guess it to be approximately 50 per cent enolized in the solvent used in this investigation. MEYER[17] reports the enol content of acetylacetone to be 79 per cent at 20°C in chloroform. Assuming this to be correct, and making reasonable estimations for the enol contents of trifluoro[8] and hexafluoroacetylacetone of ~95 per cent and ~100 per cent, respectively, one obtains the following values:

Enol of	Approx. per cent enol	λ_{max}	Approx. ϵ_{max} for enol
Acetylacetone	73–79	280	12,500 ± 500
Trifluoroacetylacetone	90–10)	284	11,100 ± 600
Hexafluoroacetylacetone	100	273	7,800

While these values are not precise, one can safely draw from them the conclusion that an increase in the electron-donating power of the groups R and R′ produces a corresponding increase in the intensity of K-absorption. This point is borne out by other substitutions as well. Taking the degree of enolization into account, one finds that when R is $-CH_3$, the K-band intensities for various R′-groups increase in the order $-CF_3 < -CH_3 < -OC_2H_5 < -N(C_2H_5)_2$.

The wavelength shifts with fluorine substitution are what one would expect an increase when a strong electron-attracting group is placed on one end of a conjugated

[16] A. GILLAM and E. S. STERN, *An Introduction to Electronic Absorption Spectroscopy in Organic Chemistry*, Edward Arnold Ltd., London, England (1954).
[17] K. H. MEYER, *Ber.*, **45**, 2843 (1912).

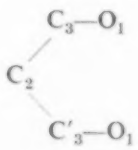
system, and a decrease when such electron-attracting groups are placed on both ends of the system.

The spectrum of acetylacetone given in Fig. 2 is in rough agreement with that given by HASZELDINE *et al.*,[10] and with ACLY and FRENCH[18] for alcohol solutions. Close agreement would not be expected in view of the wide variation with solvent of both frequency and intensity of β-dicarbonyl compounds reported by HASZELDINE *et al.*[10] Subject to the same qualifications, the absorption curves of ethylacetoacetate and of ethyltrifluoroacetoacetate given in Fig. 3 and Table 2 agree with the values reported previously.[10] In the present work, however, no secondary absorption band at higher wavelength was observed for ethyltrifluoroacetoacetate, as was reported for this substance in cyclohexane.[10] It is of interest to note that an increase in intensity is produced by a modification of the structure of ethylacetoacetate. In the case of the trifluoromethyl analogue, the effect is probably due to an increase in the degree of enolization of the compound. On the other hand, the intensity increase, accompanied by an increase in λ_{max}, observed for N,N-diethylacetoacetamide, is due to the effect on a conjugated system of replacing an electron-donating group, $-\ddot{O}-C_2H_5$, by a stronger electron-donating group, $\ddot{N}(C_2H_5)_2$.

The ultraviolet absorption spectra of *bis*-acetylacetono-Cu(II), and of its two fluoro analogues, shown in Fig. 4, show some resemblance to those of the ligands themselves. The main absorption band of the keto enol seems to be considerably intensified in the chelates, and to be split more clearly into double bands. Furthermore, there seems to be a weaker K-type band at lower wavelength, although the maxima are below the range of the measurements for the fluorinated chelates.

In reference to the shift to lower frequencies ($\sim$2800 cm^{-1} decrease) of the main ultraviolet band of acetylacetone anion upon replacement of H^+ by Cu^{++}, it is interesting to see what a crude theoretical calculation predicts. We calculate, by the LCAO molecular orbital method, an electron distribution for the ground and first excited states of acetylacetonate ion. Then, supposing the dominant effect of replacing H^+ by Cu^{++} to be increased coulombic interaction of cation and anion due to the additional cation charge, we compute the effect of this change upon the difference in energy between the ground and the first excited state.

(a) *LCAO-MO treatment*: We consider the pi-system of five p_z-orbitals containing six electrons for the pictured



skeleton, symmetry C_{2v}. Symbols are defined as usual:

$H_{ij}(=H_{ji}) \equiv \int \psi_i^* H \psi_j d\tau$, where H is the Hamiltonian for the system and ψ_i the p_z eigenfunction of atom i. Let us neglect all overlap integrals and all integrals

[18] H. E. ACLY and H. S. FRENCH, *J. Amer. Chem. Soc.*, **49**, 847 (1927).

connecting non-adjacent atoms. The secular equation is factored into a cubic and a quadratic by forming combinations of the ψ_i as follows:

$\psi_a \equiv (\psi_1 - \psi'_1)/\sqrt{2}$; $\psi_b \equiv (\psi_3 - \psi'_3)/\sqrt{2}$; $\psi_d \equiv (\psi_3 + \psi'_3)/\sqrt{2}$; $\psi_f \equiv (\psi_1 + \psi'_1)/\sqrt{2}$

$$\begin{vmatrix} H_{22}-W & \sqrt{2}\,H_{23} & O & & & \\ \sqrt{2}\,H_{23} & H_{33}-W & H_{13} & & O & \\ O & H_{13} & H_{11}-W & & & \\ & & & H_{11}-W & H_{13} & \\ & O & & H_{13} & H_{33}-W & \end{vmatrix} = 0$$

is the secular equation, where the solutions, W, give the five energy levels. We take a method of choosing parameters which we have previously used and found satisfactory for computing "resonance energies" of oxygenated molecules:[19]

$$\frac{H_{13}}{H_{23}} \approx \frac{\text{C=O energy} - \text{—C—O}^- \text{ energy}}{\text{C=C energy} - \text{—C—C— energy}} \approx 1{\cdot}8$$

We first guess the coulomb integrals: $H_{33}{}^0 = H_{22}{}^0 = H_{11}{}^0 - 2H_{23}$. Then the method given by BRANCH and CALVIN[20] and used by JAFFÉ[21] and others to account for the induction effect is applied to correct these to

$$H_{ii} = \sum_k (\tfrac{1}{3})^{n_{ik}} H_{kk}{}^0$$

where $n_{ik} - 1$ is the number of atoms between i and k. Our complete set of coulomb integrals is $H_{22} = 0$; $H_{33} = 0{\cdot}52\ H_{23}$; $H_{11} = 1{\cdot}8\ H_{23}$. Solution of the secular equation yields the following set of energy levels and orbital functions:

(I) $W_{\mathrm{I}} = 3{\cdot}30\ H_{23}$; $\psi_{\mathrm{I}} = 0{\cdot}264\ \psi_2 + 0{\cdot}617\ \psi_d + 0{\cdot}741\ \psi_f$

(II) $W_{\mathrm{II}} = 3{\cdot}09\ H_{23}$; $\psi_{\mathrm{II}} = 0{\cdot}818\ \psi_a + 0{\cdot}577\ \psi_b$

(III) $W_{\mathrm{III}} = 0{\cdot}66\ H_{23}$; $\psi_{\mathrm{III}} = 0{\cdot}754\ \psi_2 + 0{\cdot}352\ \psi_d - 0{\cdot}555\ \psi_f$

(IV) $W_{\mathrm{IV}} = -0{\cdot}75\ H_{23}$; $\psi_{\mathrm{IV}} = 0{\cdot}578\ \psi_a - 0{\cdot}817\ \psi_b$

(V) $W_{\mathrm{V}} = -1{\cdot}64\ H_{23}$; $\psi_{\mathrm{V}} = 0{\cdot}607\ \psi_2 - 0{\cdot}705\ \psi_d + 0{\cdot}368\ \psi_f$

From the orbital functions is obtained the electron density distribution for an electron in any orbital:

		Oxygen 1 or 1′	Carbon 3 or 3′	Carbon 2
e^- Density in	ψ_{I}	0·274	0·191	0·070
	ψ_{II}	0·334	0·166	0
	ψ_{III}	0·154	0·062	0·569
	ψ_{IV}	0·166	0·334	0
	ψ_{V}	0·068	0·248	0·368

[19] R. L. BELFORD, Ph.D. thesis, University of California, Berkeley (1955); University of California Radiation Laboratory Report UCRL-3051.

[20] G. E. K. BRANCH and M. CALVIN, *The Theory of Organic Chemistry*, Prentice-Hall, Inc., New York, (1941).

[21] H. H. JAFFÉ, *J. Chem. Phys.*, **20**, 279 (1952).

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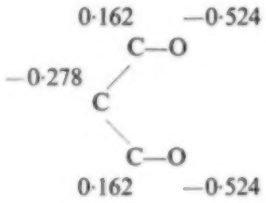
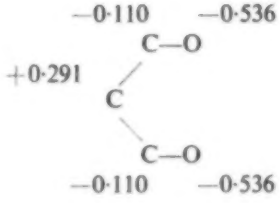
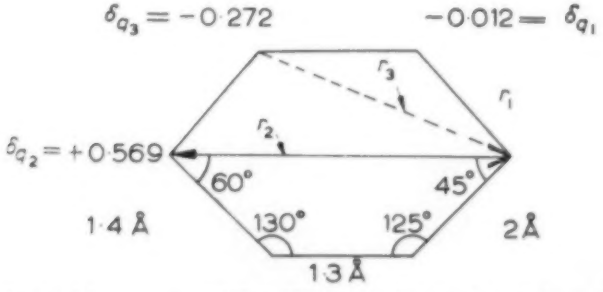
Six electrons would fill I, II, III with resulting ground-state distribution of the single anion charge as follows:



The first excited state would have I and II filled, III and IV each half-filled, with a resulting charge distribution



(b) *Electrostatic effect*: From the foregoing we take the differences in charge density between the first excited and ground states for the anion, and place a single positive charge as shown below:



The change of transition energy (III → IV) upon increasing cation charge by one unit is then given by

$$\Delta E = \left(2\frac{\delta_{q_1}}{r_1} + 2\frac{\delta_{q_2}}{r_3} + \frac{\delta_{q_2}}{r_2}\right) e^2;$$

for the geometry and δq's shown above $\Delta E_{\text{calc}} = -3200\ \text{cm}^{-1}$. The observed shift of $-2800\ \text{cm}^{-1}$ agrees fantastically well. It should be mentioned that if one performs the above calculation assuming that all exchange integrals have the same value, and that all coulomb integrals have the same value (i.e., ignoring the differences between carbon and oxygen), one obtains a calculated shift of $\Delta E_{\text{calc}} = -2500\ \text{cm}^{-1}$. Thus it appears that the treatment we use will give the observed direction and order of magnitude for the shift regardless of chosen values for the integrals (within reasonable limits, of course).

For the copper(II) chelates of the β-keto esters and amide illustrated in Fig, 3, the spectra resemble those of the ligands much more closely than is the case with the

β-diketones. Here, also, the effect of the metal is to intensify the absorption bands of the ligand and to shift them to longer wavelengths.

It is interesting to observe the spectrum, in this range, of the calcium chelate of ethylacetoacetate (Fig. 3). It resembles, both in intensity and band placement, that of the corresponding Cu chelate. This unmistakably points to the origin of the ultraviolet bands of the chelates as transitions in the enolate ions; charge-transfer spectra would surely exhibit drastic changes upon the replacement of Cu^{++} by Ca^{++}

The absorption spectra of the copper(II) chelates in the visible region, shown in Figs. 5 and 6, clearly indicate that the influence of substitution by *tri*-fluoromethyl groups in the ligand is to shift the absorption bands to longer wavelengths, thus passing more light in the low-wavelength region and accounting for the typically green colour of copper chelates of fluorinated ligands. This shift of the absorption bands increases as the number of trifluoromethyl groups increases, and thus correlates with a decrease in the stability of the metal chelate.[22]

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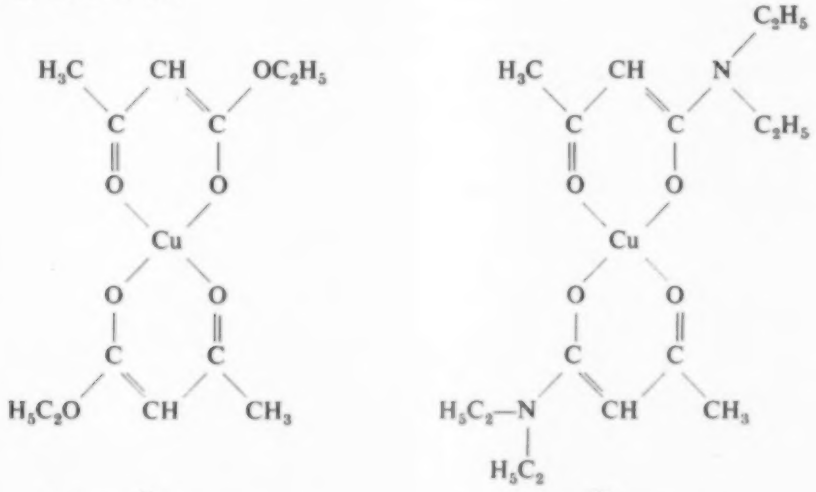
Another interesting inference may be drawn from the similarity of the spectra of the copper(II) chelates of ethylacetoacetate and N,N-diethylacetoacetamide. The fact that these curves are almost superimposable indicates that the copper(II) ion is bound only through the oxygen atoms of both ligands, as indicated by formulas Va and Vb:



Va
Bis-ethylacetoacetato-Cu(II)

Vb
Bis-N,N-diethylacetoacetamido-Cu(II)

It is seen that all of the copper chelate spectra in the visible region consist of at least two overlapping absorption bands. We believe that these are transitions between *d*-orbitals of the Cu(II) ion; the strong molecular field of the ligands partially removes the 3*d*-orbital degeneracy, permitting transitions in the visible. The two strong bands which appear for chloroform solutions of the molecules reported in this paper are likely the transitions of the hole in configuration 3*d* from the ground state, the d_{xy} orbital (if we consider ligands to be centred near the lines $x = y$ and $x = -y$), to the

[22] An increase in the acidity of the ligand, and a decrease in the affinity for Cu(II) ion, was demonstrated by CALVIN and WILSON[9] to accompany the replacement of one methyl group of acetylacetone by a strongly electron-attracting CF_3 group. It is believed that the replacement of the second methyl group will further decrease the donor power of the ligand.

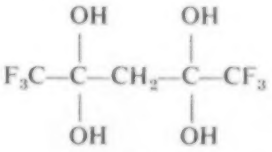
higher-energy d-orbitals, d_{xz}, d_{yz}, and $d_{x^2-y^2}$. The supposition that such transitions are responsible for the visible and near infrared absorption bands of the transition metal hydrates as well as some complex ions has been under investigation by several workers very recently.[19, 23]

It will be shown in a later paper that if the visible chelate absorption is of this sort, a decrease in donor base strength and covalent bonding tendency such as one expects from the series acetylacetone, trifluoroacetylacetone, hexafluoroacetylacetone, should cause a shift of both bands to the red and a slight increase in the ratio of wavelength of the higher wavelength band to that of the lower. For the acetylacetone series this seems to hold true. Upon passing from ethylacetoacetato-Cu(II) to the corresponding trifluoro derivative, one notes the proper shift of both bands to the red; their ratio appears to be little changed.

We have noticed that the visible absorption spectra of some of the Cu(II) chelates exhibit interesting solvent effects. These will be reported in another paper.

Infrared Spectra

For the free ligands, acetylacetone and the corresponding trifluoro and hexafluoro analogues, there is an OH-stretching vibration indicating strong enolization of one of the carbonyl groups. It is interesting that the influence of one trifluoromethyl group results in a shift of the OH band from 3550 cm^{-1} in acetylacetone to 3360 cm^{-1} in the trifluoromethyl derivative. This correlates with the fact that the enol of trifluoroacetylacetone is more acidic than that of acetylacetone itself. The further shift of the OH band in anhydrous hexafluoroacetylacetone to 3120 cm^{-1} is then just as one should expect. In the dihydrate of hexafluoroacetylacetone there are four hydroxyl groups, as indicated by Formula VI, which result in a very intense broad band at 3330 cm^{-1}.



VI
Hexafluoroacetylacetone dihydrate

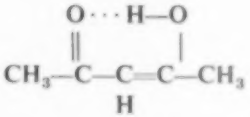
Other bidentate ligands show a similar effect of the trifluoromethyl group in displacing the OH-bond vibration to longer wavelengths. Thus the enol band of ethylacetoacetate (3550 cm^{-1}) is displaced to 3360 cm^{-1} in the trifluoromethyl derivatives.

Additional evidence for the assignment of these absorption bands to OH-stretching vibrations may be found in the complete absence of these bands in the spectra of the corresponding metal chelate compounds. Since all the enolic hydrogens are replaced by metal ions in the chelates, as is indicated by Formula II, it is apparent that all of the OH bands should disappear.

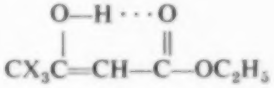
All of the ligands have absorption frequencies which may be assigned to free

[23] (a) L. E. ORGEL, *J. Chem. Soc.*, 4756 (1952).
(b) O. HOLMES, Ph.D. Thesis, University of California (1955).
(c) C. J. BALLHAUSEN, *K. Danske Videnske. Selsk., mat-fys. Medd.* **29**, 4 (1954).
(d) J. BJERRUM, C. J. BALLHAUSEN, and C. K. JORGENSEN, *Acta Chem. Scand.*, **8**, 1275 (1954).
(e) B. R. MCGARVEY, private discussions.

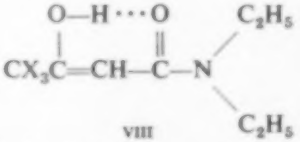
carbonyl groups, with shifts to higher (or lower) frequencies when a CF_3 group is present. Thus the normal carbonyl frequencies, 1708 and 1725 cm^{-1}, of acetylacetone are shifted to 1775 cm^{-1} and to 1745 cm^{-1} in trifluoroacetylacetone; to 1790 cm^{-1} and to 1765 cm^{-1} in hexafluoroacetylacetone. For all three ligands there is a strong, broad band, 70 to 90 cm^{-1} below the free carbonyl bands, which must be due to the conjugated, hydrogen-bonded carbonyl group characteristic of the enolic form of the β-diketone:



Since the free carbonyl frequencies of ethylacetoacetate and the corresponding amide should be close to that of acetylacetone, the 1720-cm^{-1} bands may be given this assignment. In ethylacetoacetate, the band found at 1735 cm^{-1}, 15 cm^{-1} above the free carbonyl band, has been assigned to the ester carbonyl. The highest carbonyl frequency of ethyltrifluoroacetoacetate, found at 1650 cm^{-1}, may possibly be assigned to the ester carbonyl group, and the next lower frequency, 1608 cm^{-1}, to the free carbonyl vibration. In the case of acetoacetic acid diethylamide, there can be no ester carbonyl bands, in agreement with the observed spectra. The frequency observed at 1640 cm^{-1} may be assigned to the typical amide I frequencies (tertiary amide). The lowest of the three carbonyl frequencies observed for each ester and amide may be assigned to the H-bonded (chelated) form of the ester or amide carbonyl, according to Formulas VII and VIII, where X may be H or F. These frequencies appear at about 100 cm^{-1} lower than for the corresponding ester carbonyl, and from 120 to 140 cm^{-1} below the frequency assigned to the amide carbonyl group. For acetylacetone and ethylacetoacetate our assignments agree with those of BELLAMY and BEECHER.[24]

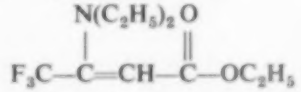


VII



VIII

Note: In the case of the ethylester of diethylamino trifluorocrotonic acid, the 1688-cm^{-1} line may be assigned to ester carbonyl (reduced by $-CF_3$ group and conjugation from normal position), and the 1638-cm^{-1} line to a C=C stretch of the crotonyl structure, corresponding to the formula:



An apparent anomaly, assuming the correctness of these tentative assignments, is the influence of CF_3 substitution on the carbonyl frequencies. In acetylacetone, a shift to higher frequencies is observed, whereas in ethylacetoacetate there is a very strong shift to lower frequencies. The corresponding shifts of the H-bonded (chelated) carbonyl frequencies, resulting from fluorine substitution, occur in the same direction, and are of similar magnitude, as the shifts in the free carbonyl frequencies.

[24] L. J. BELLAMY and L. BEECHER, *J. Chem. Soc.*, 4487 (1954).

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It is interesting that no C=C stretching frequencies have been assigned for the ligands, in analogy with the assignment of the 1633-cm^{-1} line of acetylacetone to this group. In all cases, however, other strong bands have appeared where this band would normally be expected, and the observed absorption bands may therefore be considered as combinations of the two component bands.

The bands observed in the 1300- to 1500-cm^{-1} region of the spectrum must be due to CH_3 and CH_2 deformation vibrations, in accordance with the observed frequencies of other compounds.

*Cu Chelate Spectra**

The metal chelate spectra given in Table 3a are characterized by the absence of normal carbonyl, ester carbonyl, and amide carbonyl absorptions. In each case the carbonyl spectrum of the ligand is replaced by metal-chelated carbonyl absorptions at much lower frequencies. The absorption bands of *bis*-acetylacetono-Cu(II) at 1582 and 1530 cm^{-1} have been assigned to chelated carbonyl and C=C stretch, respectively, by LECOMPTE *et al.*[26, 27] Thus the chelate carbonyl absorptions of *bis*-acetylacetono-Cu(II), *bis*-trifluoroacetylacetono-Cu(II), and of *bis*-hexafluoroacetylacetono-Cu(II), occur at 1582, 1615, and 1643 cm^{-1}, respectively. There seems to be an increase in frequency of the carbonyl band as the stability of the metal chelate decreases. Thus, decreased interaction of the metal with the carbonyl groups results from increased fluorine substitution in the molecule. The frequencies of the C=C stretch vibrations, on the other hand, are increased only slightly as methyl groups are replaced by trifluoromethyl groups. In the case of *bis*-hexafluoroacetylacetono-Cu(II) there is an additional band at 1565 cm^{-1} which is difficult to assign; it is likely also due to C=C stretch.

The ester and amide chelate compounds, IV-Cu, V-Cu, and VI-Cu, seem to have double chelate carbonyl bands, corresponding to the ketonic carbonyl and the ester or amide carbonyl of the ligands. The 1600-cm^{-1} band of the ethylacetoacetate chelate has been assigned to the ester carbonyl chelated to the Cu(II) ion, and the lower-frequency band at 1555 cm^{-1} must correspond to the chelated ketonic carbonyl group. The frequencies of both of these bands are therefore strongly shifted ($\sim$150 cm^{-1}) to lower frequencies by co-ordination with the metal ion. Another band at 1538 cm^{-1} is assigned to a C=C stretch vibration, analogous to the corresponding bands in the acetylacetone derivatives.

The frequency assignments made for *bis*-ethyltrifluoroacetoacetato-Cu(II) are completely analogous, with the exception that all the frequencies are somewhat higher than those of the ethylacetoacetate chelate. The shift to higher frequencies is much greater for the chelated ketonic carbonyl than for the chelated ester carbonyl, as would be expected from the position of the trifluoromethyl group. The C=C stretch frequency undergoes the smallest shift. The carbonyl frequencies of the N,N-diethyl-acetoacetamide chelate are considerably lower than the corresponding values for the

* Attention is called to the work of BELLAMY and BRANCH[25] on infrared spectra of $CHCl_3$ solutions of some metal chelates. Solution spectra for such chelates are not directly comparable with solid spectra, we feel.

[25] L. J. BELLAMY and R. F. BRANCH, *J. Chem. Soc.*, 4491 (1954).
[26] J. LECOMPTE, *Discussions Faraday Soc.*, No. 9, 125 (1950).
[27] C. DUVAL, R. FREYMAN and J. LECOMPTE, *Bull. Soc. Chim.* 106 (1952).

esters, and co-ordination with the metal ion results in a smaller frequency decrease ($\sim$75 cm^{-1}) for the amide than was observed for the corresponding esters.

As in the case of the free ligands, a number of the absorption bands in the 1300- to 1500-cm^{-1} region must be due to CH_2 and CH_3 deformations. Many of these bands are missing, however, because of the interference of two strong nujol bands in this region of the spectrum.

The authors would emphasize that some of their assignments of infrared frequencies may be in error; especially where two or more bands lie fairly close together, it is often impossible to decide how the likely assignments for that region should be distributed among them. However, it is felt that the general features of these spectra and the structure inferences drawn from them cannot be gross misinterpretations. The assignments have been examined quite carefully for consistency with known spectra whose interpretations are clear. A parallel infrared spectral study of the ligands and their chelates with appropriate isotopic substitutions might prove valuable in making assignments.

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J. Inorganic and Nuclear Chemistry 1956, Vol. 2, pp. 32–37. Pergamon Press Ltd., London

CYCLOPENTADIENYL-TRIETHYLPHOSPHINE-COPPER(I) AND BIS-CYCLOPENTADIENYLMERCURY(II)

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(*Received* 3 *May* 1955)

Abstract—The compound $C_5H_5Cu\ P(C_2H_5)_3$ has been prepared by the reaction of cyclopentadiene and triethylphosphine on cuprous oxide; it is a white crystalline solid stable to water.

The compound $(C_5H_5)_2Hg$ has been prepared by the reaction of mercuric chloride with sodium cyclopentadienide in tetrahydrofuran; it is a yellow solid which is stable towards water but decomposes readily thermally and in light.

The chemical properties, ultraviolet and infrared spectra of these compounds are described, and are compared with those of cyclopentadienyl-trimethylsilicon and some "sandwich bonded" cyclopentadienyl compounds.

1. INTRODUCTION

SOME years ago,[1] a study was made of numerous organometallic compounds which are soluble in petroleum fractions. Among the compounds reported was a "cuprocyclopentadiene-tri-*n*-propylphosphine." This substance was prepared by the reaction of tri-*n*-propylphosphine and cyclopentadiene with cuprous oxide in petroleum solution; the mixture was heated and water was eliminated. After filtration, the lower boiling constituents were removed and the residue, which was soluble in petroleum, was reported to have the formula $CuC_5H_5 \cdot 2(C_3H_7)_3P$. No purification or analysis of the product was recorded, nor were any of its properties. However, this work appears to be the first report of the preparation of a cyclopentadienyl compound of a transitional metal.

In view of the recent interest in cyclopentadienyl compounds of transitional metals, we have attempted to characterize a cyclopentadienyl copper compound. We have been unable to repeat VAN PESKI and MELSEN'S work with tri-*n*-propylphosphine, but using their preparative method with triethylphosphine, we have confirmed that a compound $C_5H_5CuP(C_2H_5)_3$ is formed.

Attempts to prepare cyclopentadienyl copper derivatives from both cuprous and cupric halides by the amine method,[2] by the reaction of the copper halides with C_5H_5MgBr and C_5H_5Na in tetrahydrofuran solution, and attempts to carry out the Van Peski and Melsen reaction using amines, phosphorus tri-isocyanate, triethylphosphite, etc., have all failed. Further, attempts to substitute the triethylphosphine in $C_5H_5CuP(C_2H_5)_3$ by carbon monoxide, phosphorus trichloride, and other phosphorus compounds have also failed; this suggests that, as is found with other cuprous compounds, stable derivatives are not formed with ligands which have pronounced acceptor properties, although the donor atom may be required to have weak acceptor properties in the present case.

[1] A. J. VAN PESKI and J. A. MELSEN, U.S. Patent 2,150,349.
[2] J. M. BIRMINGHAM, D. SEYFERTH, and G. WILKINSON. *J. Amer. Chem. Soc.* **76**, 4179 (1954).

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2. THE STRUCTURE OF CYCLOPENTADIENYL-TRIETHYLPHOSPHINE-COPPER(I)

It has been noted previously,[3] that the cyclopentadienyl group can be bonded to a metal atom by a "sandwich bond" for transitional metals which have a suitable *d*-orbital available for overlap with a π-orbital of the C_5H_5 ring,[4] by an ionic bond between the metal atom and the cyclopentadienide ion, $C_5H_5^-$ or thirdly, by a localized metal to carbon bond. The nature of the metal-ring bond in $C_5H_5CuP(C_2H_5)_3$ is now discussed in these terms.

(a) *A "Sandwich Bond"*—Several mononuclear cyclopentadienyl metal compounds with carbon monoxide and nitric oxide as ligands have been described,[5, 6] in which the C_5H_5 ring is unequivocally bonded to the metal atom by a "sandwich bond." By analogy, copper(I) might be expected to form compounds of the type C_5H_5CuR, where R is some ligand capable of donating two electrons to the metal atom. The copper atom would then be isoelectronic with the nickel atom in C_5H_5NiNO. Such "sandwich bonding" would require the use of a 3*d*-orbital of the copper atom. Since the normal structure of the cuprous state is $3d^{10}$, one of the *d*-orbitals would have to be freed in order to form a "sandwich bond" to copper(I).

While rigorous chemical proof that the copper-ring bond is *not* of the "sandwich bond" type is lacking, the infrared spectrum, and particularly the ultraviolet spectrum, shows little resemblance to the corresponding spectra of other mononuclear cyclopentadienyl metal compounds;[7] these points are discussed below.

(b) *An Ionic Bond*—Ionically bonded compounds are those of highly electropositive elements, e.g., C_5H_5Na, $(C_5H_5)_3La$,[3] and of the special case of manganese, $(C_5H_5)_2Mn$.[8] In view of the electropositivity of copper and the tendency of cuprous compounds when ionized to disproportionate into copper and the cupric ion, an ionic bond between the metal and the $C_5H_5^-$ ion seems unlikely. The failure of the compound to react with water and its ready solubility in petroleum ether are not in keeping with ionic character in the molecule.

(c) *A Localized Metal-Carbon Bond*—The only compounds previously reported which appear to be of this type are the cyclopentadienylalkylsilanes.[9] Since the infrared and ultraviolet spectra of cyclopentadienyltrimethylsilicon were rather different from those of $C_5H_5CuP(C_2H_5)_3$, we prepared the mercury compound, *bis*-cyclopentadienylmercury $(C_5H_5)_2Hg$, for further comparison. In the mercury compound there is no possibility of "sandwich bonding" since suitable *d*-orbitals are not available, and any possibility of ionic bonding is very remote. The compound does indeed appear to have a localized metal-carbon bond as is shown by the characterization of the maleic anhydride adduct.

The ultraviolet absorption spectra of several compounds relevant to this discussion are shown in Fig. 1. The ultraviolet absorption spectrum of cyclopentadienyltrimethylsilicon is quite similar to that of cyclopentadiene, both compounds showing peaks at 2420 Å ($\varepsilon = 3000$) and 2410 Å ($\varepsilon = 3120$) respectively, which are characteristic of the conjugated diene system.

[3] G. WILKINSON and J. M. BIRMINGHAM, *J. Amer. Chem. Soc.*, **76**, 6210 (1954).
[4] (a) W. MOFFITT, *J. Amer. Chem. Soc.*, **76**, 3386 (1954). (b) D. DUNITZ and L. E. ORGEL, *Nature*, **171**, 121 (1953); *J. Chem. Phys.*, **23**, 954 (1955).
[5] T. S. PIPER, F. A. COTTON, and G. WILKINSON, *J. Inorg. Nucl. Chem.*, **1**, 165 (1955).
[6] T. S. PIPER and G. WILKINSON, *ibid.*
[7] F. A. COTTON, A. D. LIEHR and G. WILKINSON, *J. Inorg. Nucl. Chem.*, **1**, 175 (1955).
[8] G. WILKINSON, J. M. BIRMINGHAM, F. A. COTTON, *J. Inorg. Nucl. Chem.* (in press).
[9] K. C. FRISCH, *J. Amer. Chem. Soc.*, **75**, 6050 (1953).

Bis-cyclopentadienylmercury also has a band in this region at 2370 Å, but the intensity is too high, $\varepsilon = 22{,}700$, to be attributable to the diene system. It may be noted that diphenylmercury has a band at 2300 Å ($\varepsilon = 27{,}500$), which is much too intense to be attributable to absorption in the phenyl groups in this region of the spectrum. It seems likely therefore that these strong absorption bands are charge transfer bands associated with the mercury-to-carbon bond. The second band in the spectrum of *bis*-cyclopentadienylmercury at 2860 Å ($\varepsilon = 12{,}300$) may arise from interaction between the mercury-to-carbon bond and the diene system. This interaction would lead to an intensification and a bathochromic shift of the diene band system.

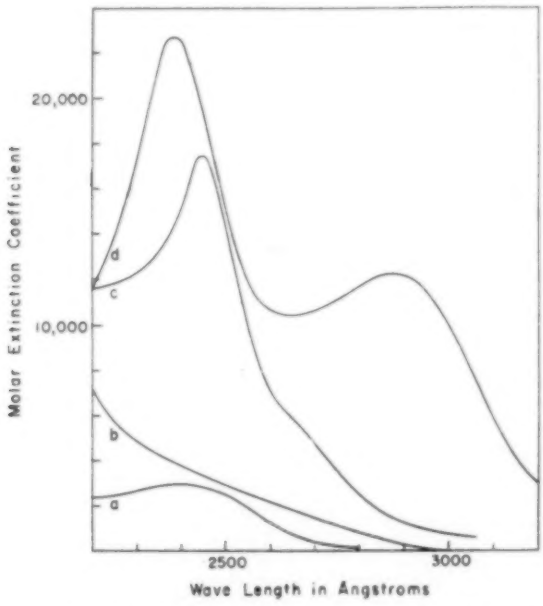

FIG. 1.—Ultraviolet absorption spectra in cyclohexane.
(a) $C_5H_5(CH_3)_3Si$
(b) $(C_5H_5)_2Fe$
(c) $C_5H_5CuP(C_2H_5)_3$
(d) $(C_5H_5)_2Hg$.

In contrast to *bis*-cyclopentadienylmercury, ferrocene and the mononuclear "sandwich bonded" cyclopentadienyl metal derivatives show no intense absorptions in this region. The spectrum of copper compound $C_5H_5CuP(C_2H_5)_3$, however, resembles that of the mercury compound and has a band at 2440 Å ($\varepsilon = 17{,}500$) and a shoulder at ~2700 Å. In the copper compound there is an additional factor which is not present in the case of the mercury compound, and that is the possibility of charge transfer absorption associated with the copper-to-phosphorus bond. The spectrum of triethylphosphine cuprous iodide, $[CuIP(C_2H_5)_3]_4$, shows generally rising absorption with shorter wavelengths; at 2450 Å, $\varepsilon = 21{,}800$ or 5400 per copper atom. Thus the high intensity band in the copper spectrum may be accounted for as the sum of the absorptions of the copper-to-phosphorus and copper-to-carbon bonds. If we

accept, as seems reasonable, the view that the 2860-Å band in $(C_5H_5)_2Hg$ is attributable to the diene system, intensified by interaction with the mercury-to-carbon bond, the band in the spectrum of the copper compound at 2700 Å may well arise in a similar way.

The evidence on the nature of the C_5H_5 ring-to-copper bond obtained from infrared absorption measurements (Fig. 2) is inconclusive and largely negative in character. By comparison with $[CuIP(C_2H_5)_3]_4$, the bands in the spectrum of $C_5H_5CuP(C_2H_5)_3$ at 2950, 1720, 1460, 1420, 1380, 1263, 1240, and 1047 cm^{-1} appear to be due to the copper-phosphine system. The bands characteristic of the mononuclear cyclopentadienyl carbon monoxide and nitric oxide metal compounds[5] at 1430 (m) and 800–850 (vs) cm^{-1} are absent. Although there is little similarity between the spectra of cyclopentadienyltrimethylsilicon, *bis*-cyclopentadienylmercury, and $C_5H_5CuP(C_2H_5)_3$, they all possess a band at 1610–1640 cm^{-1} which may be attributable to the carbon-carbon double-bond stretching mode.

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Chemical evidence for the nature of the C_5H_5 ring-to-copper bond is indecisive. Although $C_5H_5CuP(C_2H_5)_3$ reacts with maleic anhydride to give red precipitates, triethylphosphine itself also reacts with the anhydride; we have accordingly not been able to firmly characterize an adduct of the copper compound. With ferrous chloride in tetrahydrofuran, the copper compound reacts more readily than does the mercury compound to form ferrocene, while the silicon compound, as might be expected from the greater strength of the carbon-to-silicon bond, does not react at all. While the reaction with ferrous chloride has been shown[8] to be typical of ionically bonded cyclopentadienides, a similar reaction of compounds with weak metal to C_5H_5 ring bonds of the localized type is not unexpected, although the yields may not be quantitative and the reactions may be slower in this case.

While unaffected by water, with dilute hydrochloric acid both the copper and mercury compounds react to form cyclopentadiene; the ionic cyclopentadienides react vigorously even with water, and the "sandwich bonded" compounds such as $C_5H_5Mn(CO)_3$ or C_5H_5NiNO are unaffected by dilute acid. The copper and mercury compounds do not react with carbon dioxide.

While we do not feel that the evidence is unequivocal, the chemical and physical properties of $C_5H_5CuP(C_2H_5)_3$ are consistent with the formulation where the metal-to-ring bond is of the localized type as in *bis*-cyclopentadienylmercury.

3. EXPERIMENTAL

Cyclopentadienyl-triethylphosphine-copper(I)

Cuprous oxide was prepared by hydrazine reduction of aqueous cupric sulphate.[10] The dried solid (7·2 g) was suspended in a mixture of petroleum ether (30–60°) (150 ml), and cyclopentadiene (20 ml). Triethylphosphine (20 ml), prepared from ethylmagnesium bromide and phosphorus trichloride,[11] was added dropwise with stirring, and the mixture heated under reflux in a nitrogen atmosphere for two hours. The solvent was removed and the product dissolved in benzene. After removal of insoluble matter by centrifugation, the benzene was stripped and the product dissolved in petroleum ether. This solution was washed well with water to remove any triethylphosphine oxide. The latter is formed in high yields by the reaction of cuprous oxide and triethylphosphine, and small quantities are always present in the crude product. The petroleum fraction was dried and cooled

[10] G. BRAUER, *Handbuch der Praparaticen Anorganischen Chemie*, F. Enke, Stuttgart, pp. 755 (1954).
[11] cf. W. C. DAVIES, P. L. PEASE and W. J. JONES, *J. Chem. Soc.*, 1262 (1929).

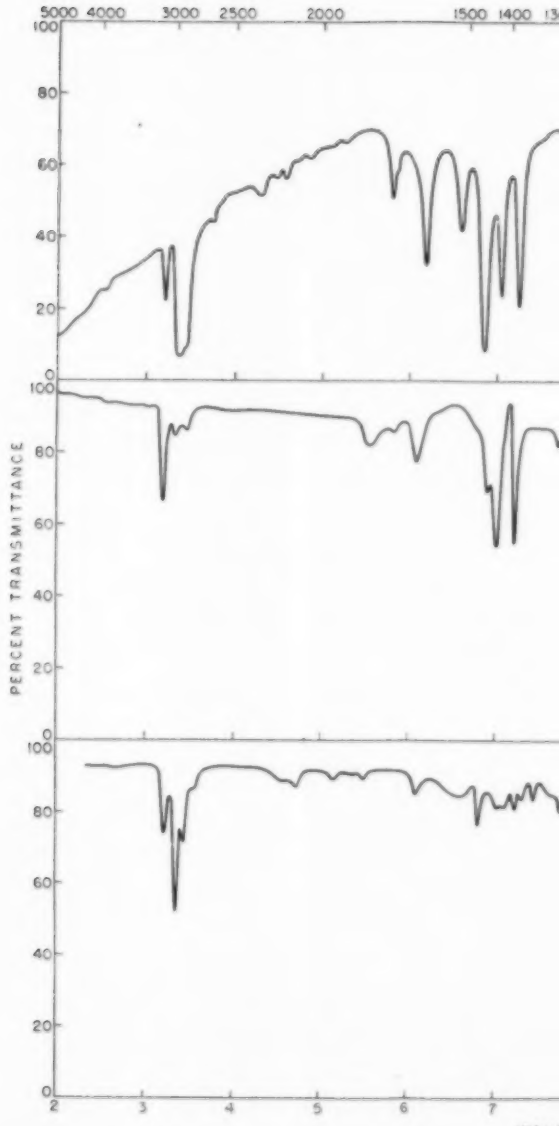
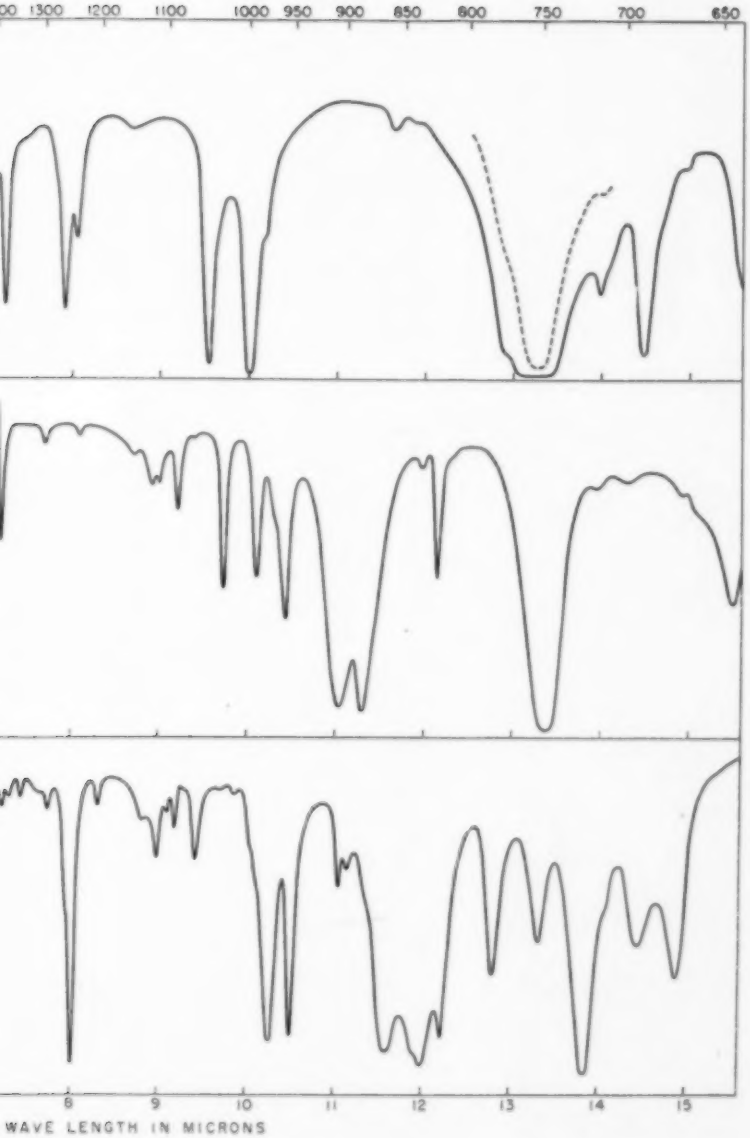


FIG. 2.—

Top: $C_5H_5CuP(C_6H_5)_3$, 21 mg/g.
Middle: $(C_5H_5)_2Hg$, 35 mg/ml in CS
(6·6–7·1 μ)
Bottom: $C_5H_5(CH_3)_3Si$, 13 mg/ml in



G. 2.—Infrared absorption spectra
mg/g. KBr in a one-inch disc.
in CS_2 (2–6 μ) and (7·1–15·5 μ) in $CHCl_3$ (6·6–6·6 μ) and in CCl_4

/ml in CS_2, $CHCl_3$, and CCl_4 as above.

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to −78°C. The white crystals were removed by centrifugation and were purified by recrystallization and by sublimation at 60°C in a vacuum system, at 10^{-3} mm Hg. Yield ~60 per cent based on cuprous oxide.

Cyclopentadienyl-triethylphosphine-copper(I) forms white acicular crystals; m.p. 127–128°C. [*Anal.* Found: C 54·6, H 8·13, Cu 25·76, P 12·69; required for $C_5H_5CuP(C_2H_5)_3$, C 53·5, H 8·17, Cu 25·73, P 12·56.] The solid is only quite slowly oxidized by air turning blue-green in a few hours time. It is insoluble in and is unattacked by water. It is soluble in and reacts with non-oxidizing dilute acids such as hydrochloric acid; the cyclopentadiene liberated was extracted with carbon tetrachloride and characterized by its infrared absorption spectrum. The compound is readily soluble in petroleum (30–60°) and in ether, benzene, and similar solvents; the solutions are quite readily oxidized by air. Although the compound does not react with carbon dioxide, it is instantaneously decomposed by carbon disulphide, triethylphosphine sulphide being formed. Rapid decomposition also occurs with chloroform and carbon tetrachloride.

The compound is soluble without reaction in pyridine and can be crystallized unchanged from triethylamine. It is decomposed rapidly by phosphorus trichloride. With carbon monoxide under pressure at room temperature there is a slow reaction, but on warming to 50°C rapid reaction occurs with decomposition to copper metal. Attempts to oxidize the compound to a cyclopentadienyl-nitric oxide copper cation with nitrous acid in ethanol led to complete disruption of the molecule. With ferrous chloride (which was prepared in a reactive form by reduction of ferric chloride with iron power) in tetrahydrofuran solution, the copper compound reacts very rapidly and almost quantitatively to form ferrocene; the latter was recovered by petroleum extraction after vacuum evaporation of the reaction mixture. The compound is diamagnetic.

Bis-cyclopentadienylmercury(II)

Sodium shot (3·5 g) in tetrahydrofuran (100 ml) was treated with cyclopentadiene (13 ml). After evolution of hydrogen ceased, the solution was cooled to −30°C and a solution of mercuric chloride (13·5 g) in tetrahydrofuran (150 ml) was added slowly. The mixture was allowed to warm to room temperature and was stirred for thirty minutes. Water (1 ml) was added to the solution at 0°C, the solvent was removed in vacuum, and the residue extracted with ether (150 ml). The ether was washed with water and dried. The product was obtained by cooling the ether solution to −78°C. It was recrystallized in the same way. Yield 3 g (20 per cent based on mercuric chloride).

The compound forms pale yellow crystals which begin to decompose at ~60°C, but which melt with decomposition at 83–85°C. [*Anal.* Required for $(C_5H_5)_2Hg$: C 36·3, H 3·04, Hg 60·6. Found: C 36·6, H 3·1, Hg 60·3.] The compound is readily soluble in ether, benzene, chloroform, carbon disulphide, and most organic solvents. It slowly decomposes on standing at room temperature even in the dark. It is insoluble in and does not react with water or bases. With dilute hydrochloric acid it dissolves, liberating cyclopentadiene. It reacts with ferrous chloride in tetrahydrofuran solution only slowly at room temperature, but rapidly on warming; ferrocene is formed quantitatively. With maleic anhydride in benzene solution at 25°C, two molecules of the anhydride are consumed per molecule of the compound and a white benzene insoluble adduct is precipitated. The precipitate was removed by centrifugation, was washed with benzene, and dried in vacuum; m.p. 163–165° (decomp). [*Anal.* Required for $C_{10}H_{14}O_6Hg$: Hg 38·0. Found: Hg 37·6.]

Cyclopentadienyltrimethylsilicon

This was prepared by a method similar to that used by FRISCH, except that sodium cyclopentadienide in tetrahydrofuran was used instead of the Grignard reagent.

Ultraviolet Absorption Spectra

These were measured in cyclohexane solution, using a Cary recording ultraviolet spectrophotometer with quartz cells. In the preparation of solutions of $C_5H_5CuP(C_2H_5)_3$, air was rigorously excluded from the solutions. The solvent was degassed and distilled in vacuum and the solutions were prepared in an inert atmosphere in a gloved box.

Infrared Absorption Spectra

These were obtained in the rock-salt region, using a Perkin-Elmer double-beam recording spectrophotometer Model 21.

In the preparation of the window of $C_5H_5CuP(C_2H_5)_3$, the grinding and pressing operations were carried out in a nitrogen atmosphere. The spectra of $C_5H_5CuP(C_2H_5)_3$, $(C_5H_5)_2Hg$, and $C_5H_5(CH_3)_3Si$ are shown in Fig. 2.

ACKNOWLEDGEMENTS

We wish to thank Professor W. MOFFITT for his helpful advice, and we are indebted to the National Science Foundation for a predoctoral fellowship (T. S. P.). Thanks are due to Dr. P. L. PAUSON for his helpful assistance in preliminary experiments on copper derivatives. This work was supported in part by the Atomic Energy Commission.

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J. Inorganic and Nuclear Chemistry, 1956, Vol. 2, pp. 38–45. Pergamon Press Ltd., London

CYCLOPENTADIENYL-NITRIC OXIDE COMPOUNDS OF CHROMIUM AND MANGANESE

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(*Received* 18 *April* 1955)

Abstract—The compound $C_5H_5Cr(NO)_2Cl$ has been prepared by the reaction of nitric oxide on the product of the reaction of $CrCl_3$ with C_5H_5Na in tetrahydrofuran solution; it has been converted to the thiocyanate $C_5H_5Cr(NO)_2(SCN)$.

The compound $(C_5H_5)_2Mn_2(NO)_3$ has been isolated from the products of the reaction of nitric oxide with manganese cyclopentadienide, $(C_5H_5)_2Mn$.

The properties and possible structures for the compounds are discussed. The compound $C_5H_5Fe(CO)_2I$ is also described.

1. INTRODUCTION

SEVERAL cyclopentadienyl-carbon monoxide compounds of transitional metals have been recently described.[1–4] The compounds, which are all diamagnetic, are mono- or binuclear for elements of odd and even atomic number respectively, e.g., $C_5H_5Mo(CO)_5MoC_5H_5$,[1] $C_5H_5V(CO)_4$,[2] $C_5H_5Co(CO)_2$,[4] $C_5H_5Fe(CO)_4FeC_5H_5$.[4] Nitric oxide may form similar compounds, and as in the case of metal carbonyls and nitrosyls, since the molecule has an odd electron, one nitric oxide will not simply replace one carbon monoxide, although the NO^+ ion will do so. Examples of such nitric oxide derivatives are C_5H_5NiNO[3] and the cation $[C_5H_5Mn(CO)_2NO]^+$ [3].

We have now prepared cyclopentadienyl-nitric oxide compounds of chromium and manganese.

2. CHROMIUM

The reaction of anhydrous chromic chloride with sodium cyclopentadienide in tetrahydrofuran solution in the mole ratio 1 : 2 leads to a green solution; from the reaction products of nitric oxide on this solution, the compound $C_5H_5Cr(NO)_2Cl$ can be isolated. This chloride has been converted to a thiocyanate.

Both of these compounds have infrared spectra closely resembling those of the mononuclear cyclopentadienyl-carbon monoxide metal compounds,[4, 13] and this fact, together with their failure to react with water or dilute acids to form cyclopentadiene, with ferrous chloride in tetrahydrofuran solution to form ferrocene, and with maleic anhydride, indicates that the metal-to-ring bond is of the "sandwich bond" type,[5, 6] as in ferrocene.

The chromium compounds undoubtedly have the same type of structure[4] as the $C_5H_5MX_3$ compounds such as $C_5H_5Mn(CO)_3$ and $C_5H_5Fe(CO)_2Cl$. For the metal atom (in this case, chromium), there will again be fourteen valence electrons (six from Cr, one from the C_5H_5 radical, six from two NO molecules, and one from Cl) to be allocated to the 3*d*-, 4*s*-, and 4*p*-orbitals of the metal atom. Since the compounds are diamagnetic, as with other mononuclear compounds of this type, only one 4*p*-orbital

[1] G. WILKINSON, *J. Amer. Chem. Soc.*, **76**, 209 (1954).
[2] E. O. FISCHER and W. HAFNER, *Z. Naturforschg.* **9b**, 503 (1954).
[3] E. O. FISCHER and R. JIRA, *ibid.* **9b**, 618 (1954).
[4] T. S. PIPER, F. A. COTTON and G. WILKINSON, *J. Inorg. Nucl. Chem.*, **1**, 165 (1955).
[5] W. MOFFITT, *J. Amer. Chem. Soc.*, **76**, 3386 (1954).
[6] J. D. DUNITZ and L. E. ORGEL, *Nature*, **171**, 121 (1953); *J. Chem. Phys.*, **23**, 954 (1955).

can be involved in metal to ligand bonding; this implies that, in these molecules, two of the 4*p*-orbitals lie at a level too high to be utilized for bonding purposes.

Experimental

Cyclopentadienyl-di-nitric oxide—chloro-chromium (O)

To sodium shot (4·6 g) in tetrahydrofuran (250 ml) was added slowly cyclopentadiene (16·5 ml); after evolution of hydrogen ceased, anhydrous chromic chloride (16 g) was added, and the mixture stirred rapidly under reflux for two hours. About 0·1 mol nitric oxide, which had been freed from other oxides of nitrogen by passing the gas through a trap cooled to −78°C, was bubbled slowly through the green solution. The solvent was removed in vacuum and the residue extracted with chloroform. The product was obtained by addition of petroleum ether (30–60°) to the filtered chloroform extract. It was recrystallized from petroleum ether-chloroform mixtures by cooling the solution to −78°C. Yield, 1·5 g.

Cyclopentadienyl-di-nitric oxide—chloro-chromium (O) forms greenish-yellow crystals which decompose without melting at ~140°C. [*Anal.* Required for $C_5H_5Cr(NO)_2Cl$: C 28·2, H 2·37, Cr 24·4, Cl 16·7, N 13·2. Found: C 28·8, H 2·8, Cr 24·4, Cl 16·6, N 12·9.] The molecular weight was determined by the isothermal distillation method[7] at 25°C in benzene solution with ferrocene as a reference; found 215, calculated 212·6.

The compound is very soluble in chloroform, moderately soluble in benzene, and slightly soluble in petroleum ether. The crystals are quite stable in air, but the yellow solutions in organic solvents decompose within a day. The compound is moderately soluble in water, giving stable yellow solutions which are acid owing to hydrolysis. The cation $[C_5H_5Cr(NO)_2]^+$ can be removed from aqueous solutions by Dowex 50 cation exchange resin, and can be recovered quantitatively by increasing the hydrogen-ion concentration. Silver nitrate precipitates silver chloride from the aqueous solutions instantaneously. In concentrated solutions, precipitates are given by silicotungstic acid and sodium tetraphenylboron; these precipitates are more soluble in water than are those of bis-cyclopentadienylmetal cations. The $C_5H_5Cr(NO)_2Cl$ can be extracted by chloroform from aqueous solutions, showing that the dissociation is only partial; the extraction is poor from basic solutions but excellent from hydrochloric acid solutions, indicating suppression of ionization and hydrolysis by the acid.

Cyclopentadienyl-di-nitric oxide—thiocyano-chromium (O)

The yellow, halogen-free solution, obtained by the action of silver nitrate on aqueous $C_5H_5Cr(NO)_2Cl$ solutions, is treated with excess sodium thiocyanate. On extraction of the solution with chloroform, the compound $C_5H_5Cr(NO)_2(SCN)$ is obtained, which is precipitated by addition of petroleum ether. It is recrystallized from petroleum ether-chloroform mixtures. The conversion of the chloride to the thiocyanate is quantitative. The compound forms well-defined crystals, which are yellow in thin section, but green in the mass; m.p. (decomp.), 165°C. [*Anal.* Required for $C_5H_5Cr(NO)_2(SCN)$: C 30·7, H 2·14, Cr 22·1, N 17·87, S 13·62. Found: C 30·67, H 2·07, Cr 22·2, N 17·81, S 13·20.] The compound dissolves readily in chloroform and benzene and is sparingly soluble in water and in petroleum ether. The solutions are yellow in colour. Other compounds similar to the thiocyanate and which are prepared in the same manner by extraction with chloroform from aqueous solutions are the *cyanide* $C_5H_5Cr(NO)_2(CN)$, the *nitrite* $C_5H_5Cr(NO)_2(NO_2)$, the *fluoride*, the *bromide*, and the *iodide*.

Infrared Spectra

The spectra were taken, using a Perkin-Elmer double-beam recording spectrophotometer Model 21 with a rock-salt prism. The spectra are similar to each other, with the exception of the additional bands due to the thiocyanate group, and to those of other mononuclear cyclopentadienyl compounds.[8] As is to be expected from the proposed symmetry of the molecules, considering only the local symmetry of the NO group,[8] two strong N-O stretching frequencies separated by about 100 cm^{-1} are observed.

[7] E. D. CLARK, *Industr. Eng. Chem.* (Anal.), 13, 820 (1941).

[8] The observed spectra of cyclopentadienyl-carbon monoxide metal compounds have been found to be consistent with this assumption,[10] and there is no reason to doubt its validity for the nitric oxide derivatives.

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$C_5H_5Cr(NO)_2Cl$; 5 mg/g in 1-in. diam. potassium bromide window: 3085 (w), 1430 (m), 1360 (vw), 1010 (m), 870 (m), 833 (vs) cm^{-1}; in chloroform solution 2 mg/ml, 1823 (vs) (NO), 1715 (vs) (NO) cm^{-1}.

$C_5H_5Cr(NO)_2(SCN)$; 5 mg/g in 1-in. diam. potassium bromide window: 3085 (w), 1440 (w, sh), 1430 (m), 1360 (vw), 1060 (m), 1020 (m), 1010 (m), 945 (m), 880 (m), 845 (m, sh), 836 (vs); in chloroform solution 2mg/ml, 2094 (vs) (CN), 1827 (vs) (NO), 1723 (vs) (NO) cm^{-1}.

Magnetism

Measurements on the solids by the Gouy method show that they are both diamagnetic compounds.

3. MANGANESE

The reaction of nitric oxide with manganese cyclopentadienide,[3, 9, 10] $(C_5H_5)_2Mn$, in tetrahydrofuran solution leads to a compound of the stoichiometry $(C_5H_5)_3Mn_2(NO)_3$.

The main facts which any structure for this molecule must accommodate are as follows.

(a) The cyclopentadienyl rings are bonded to the metal atoms. Evidence in this respect is provided by the infrared spectrum. Further, the compound shows none of the reactions of the cyclopentadienide-ion, $C_5H_5^-$; it does not react with air, and is unaffected by water. It reacts with maleic anhydride in dichloromethane solution, which suggests the possibility of a localized metal-to-ring bond, since compounds of the latter type[11] show polyolefinic behaviour.

The possibility that the C_5H_5 ring could be bonded through a nitrogen atom to the metal, or that the compound could be regarded as being derived from sodium nitrosocyclopentadienide, C_5H_5NONa,[12] may be eliminated on several grounds, one of which is the fact that on catalytic reduction with hydrogen, all the nitrogen appears as ammonia.

(b) The molecule is diamagnetic in the crystal and in solution. It is also monomeric in solution, and solutions in tetrahydrofuran are electrically non-conducting.

(c) In addition to the bands attributable to the cyclopentadienyl-metal system the infrared spectrum of the compound shows two strong bands which must be attributed to N-O stretching modes.[8] There is no notable difference between the infrared spectra in solution and in potassium bromide windows, unlike the cases of certain cyclopentadienyl-carbon monoxide-metal compounds.[13] The band, which occurs in solution at 1732 cm^{-1}, shows a weak splitting in the crystal spectrum; since only three N-O stretching frequencies are allowed for the molecule, and the band at 1510 cm^{-1} has a weak shoulder in both the crystal and solution spectra, the splitting of the 1732-cm^{-1} band in the crystal must be attributed to weak interaction between neighbouring molecules in the crystal lattice.

Considering only the spectrum of the free molecule, the band at 1732 cm^{-1} we assign to a non-bridging nitric oxide stretching-frequency. The compounds C_5H_5NiNO and $C_5H_5Cr(NO)_2Cl$, and salts of the cation $[C_5H_5Mn(CO)_2NO]^+$, show strong N-O stretching absorptions in the region 1850–1700 cm^{-1}. The presence in $(C_5H_5)_3Mn_2(NO)_3$ in solution of only a single frequency in this region suggests that there is only one non-bridging nitric oxide group. If two such groups existed in the molecule, they would have to be placed separately on the manganese atoms and have negligible

[9] G. WILKINSON and F. A. COTTON, *Chem. and Ind.* (London), **11**, 307 (1954).
[10] G. WILKINSON, J. M. BIRMINGHAM and F. A. COTTON, *J. Inorg. Nucl. Chem.* (in press).
[11] cf. K. C. FRISCH, *J. Amer. Chem. Soc.*, **75**, 6050 (1953).
[12] J. THIELE, *Ber.* **234**, 666 (1901).
[13] F. A. COTTON, A. D. LIEHR and G. WILKINSON, *J. Inorg. Nucl. Chem.*, **1**, 175 (1955).

interaction with each other; two non-bridging nitric oxide groups on the same manganese atom would be expected to give two N-O stretching frequencies with a splitting of ~100 cm^{-1} as is found in $C_5H_5Cr(NO)_2Cl$.

The second strong band (~1510 cm^{-1}) we attribute to one or more *bridging* nitric oxide groups. No compounds containing bridging nitric oxide groups have previously been characterized, although several binuclear compounds, e.g., $Fe_2(NO)_4(C_6H_5N)_3$,[14] have been reported. It may be noted that the difference between the 1732- and 1510-cm^{-1} bands is of the same order as that between non-bridging and bridging carbon monoxide groups in iron enneacarbonyl.[15] Such a splitting cannot be accounted for by any model with equivalent nitric oxide groups considered as coupled harmonic oscillators; in this case, splittings of the order of 50–100 cm^{-1} only would be expected.

We have considered various models for $(C_5H_5)_3Mn_2(NO)_3$, including ionic species, under the following assumptions: (a) that the rings are bonded to the metal atom; (b) that a C_5H_5 ring cannot act as a bridging group, since there are no suitable orbitals available for such bonding; (c) that there are both bridging and non-bridging nitric oxide groups. Many of the models can be eliminated at once on the experimental evidence available, and they will not be discussed here. In seeking a suitable model we have also been guided by the assumptions (a) that it is unlikely in view of the ionic nature of $(C_5H_5)_2Mn$[10] that a manganese atom in $(C_5H_5)_3Mn_2(NO)_3$ can be present in the divalent state in which the metal atom has the very stable $^6S_{5/2}$ configuration, (b) that it is unlikely that a nitric oxide molecule can be bonded by both the nitrogen and oxygen atoms, (c) that it is probable that the total number of electrons which have to be formally allocated to the two manganese atoms will be as similar as possible.

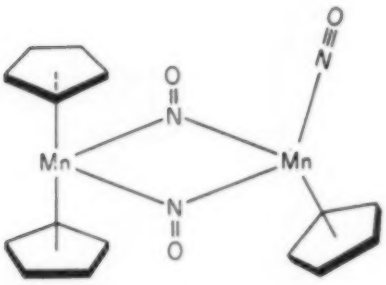
The models which seems to us best to accommodate the evidence are shown diagrammatically in Figs. 1a, b.

In these models, as indeed in all other models, one manganese atom must have two cyclopentadienyl rings bonded to it. Bearing in mind the fact that the molecule is diamagnetic, and that each nitric oxide has an odd electron, the nitrogen atoms may then, formally, be designated + and the acceptor manganese atom negatively charged; thus the formal oxidation state of the metal atom having two rings bonded to it is +3 and the oxidation state of the other atom +1. The resonating four-membered ring system of two nitrogen and two manganese atoms in the models provides the most satisfactory way in dealing with the odd electrons of bridging nitric oxide groups. The nature of such a ring is consistent with the intense colour of the compound.

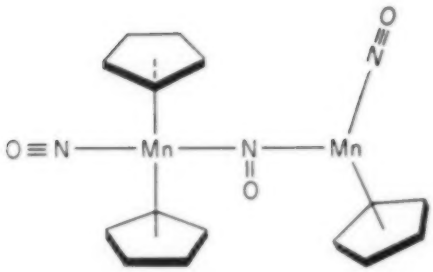
Considering the symmetry in the model (a) in respect to the infrared spectrum of the free molecule, the bridging nitric oxide groups must lie in a plane parallel to the planes of the two cyclopentadienyl rings which are bonded to the metal atom, with the N-O bonds also in this plane. The non-bridging nitric oxide group must lie in a plane which is perpendicular to the plane of the bridging nitric oxides and which bisects the N-Mn-N angle. The third cyclopentadienyl group will lie with the axis of the metal-to-ring bond in the same plane as the non-bridging nitric oxide group.

The infrared spectra in the N-O stretching region are consistent with the proposed

[14] W. Hieber and J. S. Anderson, *Z. anorg. chem.*, **211**, 132 (1933).
[15] R. Sheline and K. S. Pitzer, *J. Amer. Chem. Soc.*, **72**, 1107 (1950).



(a)



(b)

FIG. 1.—Models for $(C_5H_5)_2Mn_2(NO)_3$.

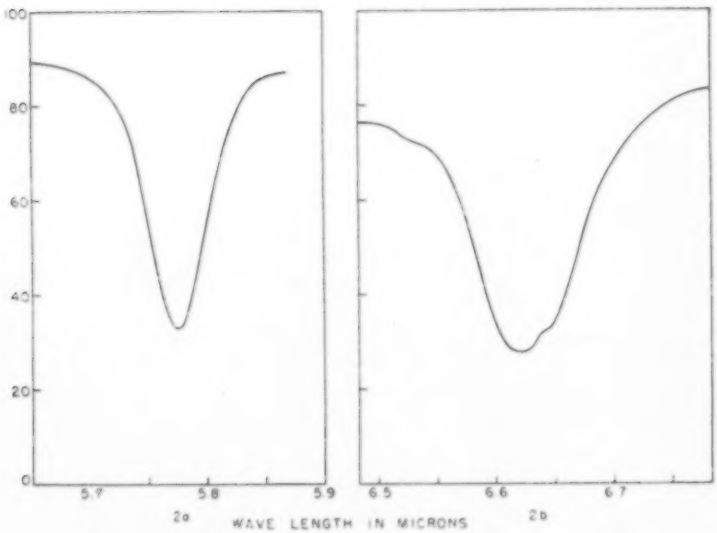


FIG. 2.—Infrared spectrum of $(C_5H_5)_2Mn_2(NO)_3$ in the N-O region.
(a) carbon disulphide solution, 4 mg/ml
(b) dichloromethane solution, 4 mg/ml

model for the free molecule. Selection rules indicate only one non-bridging N-O frequency. For the two bridging groups, the N-O frequencies will be very close together and may be superimposed. A very weak shoulder and a rather broad band are actually observed.

The electronic structures of the manganese atoms in the structures proposed for $(C_5H_5)_3Mn_2(NO)_3$ are of some interest. For the atom with a single cyclopentadienyl ring bonded to it, fourteen electrons are to be assigned; this atom is therefore isoelectronic with the atoms in the mononuclear cyclopentadienyl compounds.[4] To the manganese atom with the two cyclopentadienyl rings bonded to it must be allocated twelve electrons (Mn,7; $2C_5H_5$,2; 2 bridging NO, 3.). It will be noted that this atom thus has electrons in excess of the number assigned to the iron atom in ferrocene. According to the molecular orbital treatments of biscyclopentadienyl metal compounds such as ferrocene, the 4*p* orbitals and, in the compounds of iron and lighter elements, also the *s-d* hybrid orbital, are vacant. Whilst the latter is symmetrical about the axis of the molecule perpendicular to and passing through the centre of the C_5H_5 rings, two of the *p*-obitals, $4p_x$ and $4p_y$, will be directed outwards from the metal atom in the centre region between the rings, and will be at right angles. In the case of $(C_5H_5)_2Mn^*(NO)_2Mn(NO)(C_5H_5)$ (Fig 1a), the two bridging NO groups must be bonded to the Mn* atom using these *p*-orbitals; the N-Mn*-N angle may be expected then to approach 90°.

In the previous paragraph, and in Fig. 1a, "sandwich" bonding of *both* C_5H_5 rings to Mn* is assumed. However, the reactivity of the compound towards maleic anhydride suggests olefinic character. The only reasonable explanation then is that *one* of the rings on Mn* is σ-bonded to the metal atom (Fig. 1b). An alternative, but less satisfactory explanation is that, due to expansion of the ferrocene-like structure of Mn*, one or both of the rings have lost some of their aromatic character. Whilst proof of σ-bonding of one ring is at present lacking, we feel that Fig. 1b represents the most likely structure for the molecule. A careful examination of the C-H stretching region would confirm a σ-bonded ring: however, because of scattering in this region in KBr windows and because of the low solubility in solvents, such measurements have not been successful.

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Experimental

Manganese cyclopentadienide, $(C_5H_5)_2Mn$, was prepared by the reaction of manganous chloride with sodium cyclopentadienide in tetrahydrofuran solution.[6, 9] The compound (4·7 g) was dissolved in tetrahydrofuran (150 ml), and the theoretical quantity of nitric oxide slowly bubbled through the solution at 25°C. An exothermic reaction occurred. After removal of solvent in vacuum, the residue was extracted with chloroform (100 ml). Petroleum ether was added to the solution and the product crystallized by cooling the solution to −78°; it was recrystallized from chloroform-petroleum ether mixtures. Yield 1·3 g. (30 per cent based on $(C_5H_5)_2Mn$).

Properties

Four separate C, H, and N analyses were made by three different microanalysts:[16] manganese analyses were made colorimetrically, after destruction of the compound, by the periodate oxidation method. (*Anal.* Required for $(C_5H_5)_3Mn_2(NO)_3$: C 45·6, H 3·82, Mn 27·8; N 10·63. Found: C 45·3 ± 0·4, H 3·82 ± 0·06, Mn 27·6 ± 0·2, N 10·63 ± 0·06.) The molecular weight was determined

[16] S. NAGY, Massachusetts Institute of Technology, Cambridge, Mass. Schwarzkopf Microanalytical Laboratories 56–19 37th Avenue, Woodside 77, New York. H. MANSER, Eigd. Technische Hochschule Zurich 3, Switzerland

by the isothermal distillation method in tetrahydrofuran solution at 25°C; the compound $C_5H_5W(CO)_6WC_5H_5$ and also ferrocene were used as references. The measured value was 402; calculated for $(C_5H_5)_2Mn_2(NO)_3$, 395·2. Since there is slow decomposition of the compound in organic solvents after several days, and since several days are required to achieve equilibrium in the isothermal distillation method, a procedure of successive approximations was used. The quantities of material involved were adjusted until the vapour pressures of the solutions were equal, as shown by absence of movement in the columns during the first few days of equilibration.

The compound is a dark purple-black crystalline solid which is stable in air but decomposes on heating above 100°C even in vacuum. It is moderately soluble in chloroform, and is soluble also in benzene, acetone, tetrahydrofuran, ether, and pyridine, but is slightly soluble in carbon tetrachloride and carbon disulphide, and sparingly soluble in petroleum ether. The dark-red solutions in organic solvents decompose in air within a few hours, but in absence of air and light are stable for a week or so. The compound is insoluble in and unaffected by water. The compound is decomposed by acids and bases and also by oxidants such as nitric acid, bromine, and iodine. We have not been able to detect any cyclopentadienylmetal cations in any aqueous reaction products. Nitric oxide is liberated as such by acids.

The compound reacts with maleic anhydride in dichloromethane solution at 25°C, and is destroyed.

In tetrahydrofuran solution, the compound reacts with ferrous chloride to give a yield of only about 5 per cent of ferrocene based on the cyclopentadienyl group present in the molecule.

The compound has been hydrogenated catalytically in ethanol solution, using Adam's catalyst. The amount of cyclopentane produced was determined by extraction of the cyclopentane from the hydrogenated product with 5 ml carbon tetrachloride. This extract was washed with water to remove ethanol, and the intensity of the infrared absorption band at 1460 cm^{-1} compared with standards prepared in carbon tetrachloride solution from pure cyclopentane. The nitrogen appears as ammonia; no amines have been detected. In a typical experiment, 132 mg (1/2 millimol) of the compound was hydrogenated; the molarity of the cyclopentane solution in 5 ml carbon tetrachloride was 0·166M. Thus we obtain 2·5 mol cyclopentane per mol of the compound, a recovery of 83 per cent. Since complete recovery of the compound was impossible due to the hydrogenation technique, the yield has been compared with that in the hydrogenation of $(C_5H_5)_2TiCl_2$; here, 115 mg (½ millimol) gave a 0·170M cyclopentane solution with the mols of cyclopentane per mol of starting material 1·7, a recovery of 85 per cent. For the manganese compound the hydrogen uptake was 15 mols per mol. Thus the hydrogenation reaction appears to proceed quantitatively according to the reaction

$$(C_5H_5)_2Mn_2(NO)_3 + 15H_2 = 3C_5H_{10} + 3NH_3 + 3H_2O + 2Mn.$$

The compound does not react with carbon monoxide under pressure at 25°C either in the solid or in solution; on warming to 50°C, complete decomposition occurs with pressures of 1000 p.s.i. carbon monoxide.

The compound is diamagnetic both in the solid and in solution; measurements were made by the Gouy method.

The ultraviolet absorption spectrum in acetonitrile solution shows a peak at 2930 Å (ε = 24,000), and rising absorption at shorter wavelengths.

The infrared spectra were measured, using a Perkin-Elmer double-beam instrument in the rock-salt region. The data are as follows:

(a) in a 1-in. diameter potassium bromide window, 10 mg/g KBr, the bands are in cm^{-1}: 3085 (w), 1440 (m), 1377 (w), 1359 (w), 1084 (m), 1022 (m), 1019 (m), 1002 (w), 965 (w), 935 (m), 905 (m), 885 (m), 851 (s), 836 (s), 827 (s), 756 (vs), 720 (s, sh), 702 (s).

The frequencies we attribute to N-O stretches, not listed above, are: in the window, 1737 (vs), 1712 (w, sh), 1490 (vw, shoulder), 1500 (vs, broad) cm^{-1}; in carbon disulphide solution 1732 cm^{-1} (vs), in dichloromethane solution 1495–1500 (vw, shoulder), 1510 (vs) cm^{-1}.

4. CYCLOPENTADIENYL-DICARBON MONOXIDE-IODO-IRON(II)

In a previous paper,[4] the compound $C_5H_5Fe(CO)_2Cl$ was prepared from $C_5H_5Fe(CO)_4FeC_5H_5$ by the action of air in acid alcoholic medium. We have observed that, with iodine, oxidation of $C_5H_5Fe(CO)_4FeC_5H_5$ occurs without evolution of carbon monoxide to form a polyiodide. From the latter, $C_5H_5Fe(CO)_2I$ can be obtained.

Experimental

The compound $C_5H_5Fe(CO)_4FeC_5H_5$ (0·5 g) was dissolved in chloroform (100 ml) and iodine (0·5 g) was added. The chloroform was extracted with aqueous sodium thiosulphate solution, and the product isolated from chloroform by slow addition of petroleum ether. Yield 0·6 g (72 per cent). The compound forms black crystals m.p. 119–120°. [*Anal.* Required for $C_5H_5Fe(CO)_2I$: C 27·65, H 1·69, Fe 18·37, I 41·8. Found: C 27·74, H 1·78, Fe 18·50, I 41·3.] The compound is very slightly soluble in water, much less so than its chlorine analogue. It is somewhat soluble in petroleum ether and readily soluble in chloroform and acetone to give a brown solution. The aqueous acetone solution precipitates silver iodide only slowly upon addition of silver nitrate; in acid solutions, the precipitation is rapid and the resulting orange solution of the cation $[C_5H_5Fe(CO)_2]^+$ gives precipitates with silicotungstic acid and Reinecke's salt.

The compound is diamagnetic, and its infrared absorption spectrum closely resembles that of the chloride.[4] In potassium bromide (6 mg/g, one inch window): 3085 (w), 1428 (s), 1360 (w), 1017 (vw), 1050(w), 1007 (m), 860 (m, sh), 843 (vs, broad); in chloroform, 2 mg/ml: 2044 (vs) (CO), 2000 (vs) (CO) in cm^{-1}.

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ACKNOWLEDGEMENTS

We are indebted to Professor W. MOFFITT and Mr. A. D. LIEHR for their advice and criticism. Thanks are due to the National Science Foundation for a predoctoral fellowship (T. S. P.).

This work was supported in part by the Atomic Energy Commission.

J. Inorganic and Nuclear Chemistry, 1956, Vol. 2, pp. 46–59. Pergamon Press Ltd., London

PROTACTINIUM—I

ANALYTICAL SEPARATIONS

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(*Received* 7 *July* 1955)

Abstract—The conditions for the separation of protactinium from other elements by solvent extraction of a chloride complex by di*iso*propyl ketone have been investigated. The complex appears to contain three molecules of the solvent. Its heat of formation is small. Evidence for the existence of a sparingly soluble salt $BaPaF_7$ is advanced.

INTRODUCTION

A RECENT report on the solvent extraction of protactinium[1] and another on its separation from iron by anion exchange[2] lead us to record the methods of separation that have been developed in this laboratory during the last three years. These methods were devised for the estimation of the natural protactinium content of a large variety of materials, ranging from siliceous barium sulphate precipitates to simple solutions of uranyl salts. They have been applied to the analysis of more than a hundred samples. A combination of these procedures has been applied successfully to the separation of some two hundred milligrams of protactinium. The latter process will be described in a subsequent paper.

Recent studies of the chemistry of protactinium emphasize the necessity of handling the element in its anionic complexes, especially when tracer concentrations are concerned, otherwise losses by adsorption and irreproducible behaviour of the element are inevitable.[3, 4] The presence of soluble, colloidal, or suspended silica accentuates these difficulties. None the less, the co-deposition of protactinium on manganese dioxide is often a useful preliminary step in the isolation of the element from dilute solutions. This reaction is ineffective if the protactinium is appreciably complexed, and cannot be used, for instance, in fluoride or citrate solutions.

The complex fluoride anion, PaF_7^{2-}, is perhaps the most stable and tractable anion.[4] Hydrofluoric acid has been shown to leach protactinium from a variety of matrices,[5] and, in addition, it permits rapid isotopic equilibration of Pa^{231} and Pa^{233}, so that the latter isotope may be added to monitor separation yields. This equilibration process may be slow in solutions of the other mineral acids.[6] Three principal modes of recovery of the protactinium from these solutions have been described, in addition to the inconvenient method of displacement of the fluoride by evaporation with sulphuric acid. The protactinium may be reduced to the fluoride insoluble tetravalent state[5] and collected, for instance, on a thorium fluoride precipitate. Alternatively, it may be co-deposited on a barium fluozirconate precipitate.[7]

[1] F. L. MOORE, *Anal. Chem.*, **27**, 70 (1955).
[2] K. A. KRAUS and G. E. MOORE, *J. Amer. Chem. Soc.*, **77**, 1383 (1955).
[3] R. E. ELSON, G. MASON, D. F. PEPPARD, P. A. SELLERS, and M. H. STUDIER, *J. Amer. Chem. Soc.*, **37**, 4974 (1951).
[4] A. G. MADDOCK and G. L. MILES, *J. Chem. Soc.*, S.248 (1949).
[5] G. BOUISSIÈRES and M. HAÏSSINSKY, *Bull. Soc. Chim.* **18**, 146 (1951).
[6] A. G. MADDOCK and G. L. MILES, *J. Chem. Soc.*, S.253 (1949).
[7] W. W. MEINKE, U.S.A.E.C. Declassified Document A.E.C.D. 2750.

Finally, it has been shown possible to extract the protactinium into solvents after preferentially complexing the fluoride ion with aluminium.[3]

A number of the neutral complexes of protactinium can be extracted from aqueous solutions by immiscible organic solvents. The conditions for the extraction of the thenoyltrifluoroacetone[8] and the cupferron complexes[6] have been investigated in detail. However, since protactinium can also be extracted from mineral acid solutions by a variety of solvents, attention has been focused on these simpler processes. These extraction processes appear to have been studied in some detail, but few reports have been published in the general literature.[1, 9, 10, 11] Most of the data refer to hydrochloric or nitric acid solutions, usually in the presence of considerable amounts of dissolved salts. Four solvents—dichlorodiethyl ether,[11] di*iso*propyl carbinol and ketone,[9] and tributyl phosphate,[12] seem capable of development for an analytical separation. The first of these solvents is only suitable with aqueous solutions of moderate or high ionic strength. The last is not generally selective enough for analytical purposes. The allied problem of the separation of niobium and tantalum has been solved,[13] using solvent extraction with di*iso*propyl ketone, by varying the proportions of hydrofluoric and hydrochloric acids in the aqueous phase. A similar technique seemed possible for protactinium. This ketone does not require a salting-out agent. In this paper the conditions for the separation of protactinium from fluoride solutions on barium fluozirconate and barium fluoride precipitates are described, and a detailed study of the solvent extraction separation of the element is reported.

Protactinium can also be separated from other elements by cation, or better, anion exchange. The latter process will be the subject of a separate communication.

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EXPERIMENTAL

(a) Many of the solutions used contained free hydrofluoric acid and were therefore handled in polythene apparatus. A complete range of such apparatus—flasks, centrifuge tubes, measuring cylinders, etc.—was used. Even with other solutions in which the protactinium was present in a complex anion, it was found advisable to use polythene vessels. Considerable adsorption, or possibly ion exchange, fixes protactinium on the walls of most kinds of glass vessels from these solutions, as well as from the readily hydrolyzed cationic solutions. Losses due to this cause vary enormously with the kind of glass and its immediate history. It is better to use plastic vessels which do not suffer from this disadvantage. Polythene withstood the action of all the aqueous solutions as well as the organic solvents used. With aqueous solutions the vessels could be heated to 80–90° when necessary without ill-effect.

(b) Pa^{231} was obtained from various uranium refinery residues, as will be described in a subsequent paper.

(c) Pa^{233} was prepared by the neutron irradiation of samples of acid-soluble "thorium carbonate." This material, of uncertain composition, is reasonably thermally stable, but completely soluble in dilute nitric and hydrochloric acids. After irradiation the material was dissolved in 8N hydrochloric acid and extracted with di*iso*propyl ketone. The extract was treated with 2N hydrochloric acid when the protactinium passed back to the aqueous layer. The aqueous extract was then made 8N again and the extraction repeated. The protactinium was kept in solution in 8N hydrochloric acid

[8] R. E. Elson, U.S. National Nuclear Energy Series Div. IV, Vol. 14A, p. 125 (1954).
[9] E. K. Hyde and M. J. Wolf, National Nuclear Energy Series Div. IV, Vol. 14A, Chap. 5, Section 9.1, also Chap. 15, Section 5.2 (1954).
[10] R. C. Thompson, U.S.A.E.C. Declassified Documents MDDC 1770 (Jan.) MDDC 1897 (Feb.) (1948).
[11] A. G. Maddock and L. H. Stein, *J. Chem. Soc.*, S.258 (1949).
[12] R. E. Elson, *et. al.*; D. F. Peppard, *et al.*, U.S. National Nuclear Energy Series Div. IV, Vol. 14A, p. 125.
[13] P. C. Stevenson and H. G. Hicks, *Anal. Chem.*, **25**, 1517 (1953).

Most of the references to the United States Atomic Energy Commission publications quoted in papers (1) and (10) are not available in Cambridge.

in a polythene vessel. It was observed that losses by adsorption quickly took place on the walls of glass containers even with solutions of the chloride complex in di*iso*propyl ketone.

Better recoveries were obtained if the irradiated carbonate was dissolved in 8N hydrochloric acid 0·6N in hydrofluoric acid. This solution was nearly saturated with aluminium chloride before the first solvent extraction. The subsequent separation followed the first procedure. Neither product contained detectable amounts of thorium.

(d) α-Activities were measured with a scintillation counter. The efficiency of the counter was estimated by measuring the activity of a number of thin trays prepared by evaporating and igniting aliquots of a standard solution of A.R. uranyl nitrate solution. It was 30·5 ± 0·3 per cent. Samples were prepared for counting by the evaporation and ignition of aliquots of the solutions, or by transference of precipitates to the trays as slurries in a suitable solvent, and drying after careful distribution of the precipitate. Accurate aliquots of solutions were obtained using mercury calibrated micropipettes. A micrometer-controlled pipette ("Agla" micrometer syringe) was also used for small aliquots. The "trays" consisted of standard discs of aluminium, copper, nickel, or platinum foils. The choice of foil for a particular series of experiments depended on the nature of the solutions involved. The samples were not allowed to exceed 1 mg/cm² thickness.

(e) The β- and γ-activity of the trays used for α-measurements were determined, using an end-windowed counter with an aluminium window of about 7 mg/cm². Some early measurements were also made, using an annular liquid Geiger counter, but the decontamination of the counter was troublesome, so later measurements were made with an annular scintillation counter with a NaI/Tl crystal about 3 cm high and 2 cm diameter. In this counter the sample holder was an annular polythene vessel. This arrangement proved most satisfactory.

RESULTS

1. *Preliminary Experiments*

It was observed that, even from strongly acidic solutions that had previously been shown not to lose protactinium when centrifuged at high speed,[4] losses of Pa^{233} took place in glass vessels when tracer concentrations were used. Similar behaviour was observed with solutions of the nitrate and chloride complexes in organic solvents. Nitrate solutions were avoided, since the nitrate complex seemed to be especially prone to such behaviour. It was found that such losses were greatly reduced by the use of polythene or platinum vessels.

Since evaporation of solution was occasionally necessary, and since the trays for the estimation of Pa^{231} were to be prepared by evaporation and ignition, the possible losses of protactinium by volatilization in these processes were measured. Experiments with Pa^{233} showed that there was less than 0·5 per cent loss on evaporation of 50-ml amounts of concentrated hydrofluoric, nitric, sulphuric, and hydrochloric acid solutions to 1 ml. Distillation of hydrochloric acid containing Pa^{231} at tracer concentration showed that less than 0·1 per cent of the protactinium appeared in the distillate. It has been suggested, however, that protactinium may volatilize from mixtures of hydrochloric and hydrofluoric acids. A similar experiment with Pa^{233} at tracer concentration in the mixed acids showed the loss was less than 1 per cent. To ensure that the concentration of protactinium does not influence the loss in this system, a distillation was conducted in a polythene system at 95°C, using 25 ml of a solution containing 2·0 mg of Pa^{231}. The α-activity of the distillate could not be detected.

The loss by volatilization on ignition of the counting trays was tested, using both Pa^{233} and Pa^{231} trays. Aliquots of the tracer solution were evaporated on a number of copper and platinum discs. The trays were heated for varying lengths of time at temperatures from 80°-360°C. In no case did the activity fall more than 1 per cent.

The platinum discs were then heated to 800°C for one hour without greater loss of the activity.

The latter observation was important, since it permitted the volatilization of the active Po^{210} which might have interfered with the estimation of Pa^{231}. Samples containing Po^{210} were ignited to constant activity at 800°C.

Test experiments showed that tracer amounts of Pa^{233} could be extracted from aqueous chloride and nitrate solutions by di*iso*propyl ketone even in the absence of considerable concentrations of dissolved salts. Since the disadvantages of the nitrate solution, referred to above, quickly became apparent, further effort was diverted to chloride solutions.

2. *Co-deposition on Manganese Dioxide*

The previously reported conditions for this separation were confirmed,[6] as was its inefficiency in the presence of the strongly complexing fluoride or citrate ions. An advantage of this process was its tolerance of siliceous material in the solution. A new method of separation of this protactinium from the precipitate was developed. Leaching with hydrofluoric acid solution gave the following results.

Normality of acid	0·1	1·0	10
Per cent Pa^{233} leached out	68	94	98

3. *Behaviour in Alkaline Solutions*

Protactinium is generally co-deposited on hydroxide precipitates, and this reaction was found convenient for the concentration of the element from large volumes of dilute aqueous solutions. However, it was found necessary to avoid the use of too great a concentration of alkali hydroxide, or co-deposition became inefficient, possibly because of peptization of the protactinium. The incomplete co-deposition from ammonium carbonate solutions, previously observed,[4] was confirmed. Between 55 and 88 per cent of the Pa^{233} in hydrochloric acid solution at tracer concentration, and in the presence of iron and zirconium, was carried down by the addition of excess ammonium carbonate solution. But the same reagent only leached a small amount of the protactinium from a hydroxide precipitate. To this extent protactinium resembles thorium in its behaviour at comparable concentrations.[14] An attempted separation of tracer amounts on a carbonate precipitate formed by the addition of strong sodium carbonate solution was also unsuccessful.

At tracer concentrations true solution of the protactinium content of these precipitates needs a strongly complexing acid; indeed, only hydrofluoric acid is entirely reliable. But at higher concentrations the protactinium dissolved perfectly in concentrated hydrochloric acid.

4. *Precipitation in Fluoride Solutions*

(a) *Co-deposition on barium fluozirconate*—The conditions for the co-deposition of protactinium on barium fluozirconate from hydrofluoric acid solutions were investigated, using Pa^{233} at tracer concentrations on a 10-ml scale. Selected favourable conditions were checked at a much higher concentration with Pa^{231} as tracer and with larger volumes of solution.

[14] M. Bachelet, *Ann. Chim.*, **12**, 348 (1939).

(i) Effect of concentration of zirconium. Each solution was 2·5N in hydrofluoric acid, and the barium-zirconium concentration ratio was constant at 2·5.

Zr concentration mg/ml	2	1	0·25	0·1	0·03
Per cent Pa carried down	67	61	61	50	4·2

(ii) Effect of hydrofluoric acid concentration. Each solution contained 1mg/ml of zirconium, and the barium-zirconium concentration ratio was constant at 2·5.

HF normality	2·5	5	10	15	20
Per cent Pa carried down	61	56	36	23	0

Washing with 20N hydrofluoric acid removed 94 per cent of the protactinium co-deposited on a barium fluozirconate precipitate.

(iii) Effect of barium-zirconium concentration ratio. Each solution contained 2 mg/ml of zirconium, and was made 2·5N in hydrofluoric acid.

Ba/Zr ratio	0·5	1·5	2·5	5	10
Per cent Pa carried down	0	19	67	82	96

(iv) Time allowed for complexing of the zirconium. The published directions for this separation allow the fluozirconate mixture to stand one hour before addition of barium.[7] The desirability of this delay was tested in the following experiment. Each solution contained 2 mg/ml of zirconium, the barium-zirconium concentration ratio was adjusted to 5 and the solution was 2·5N in hydrofluoric acid.

Time elapsing between zirconium and barium additions (min)	0	12	30	90
Per cent Pa carried down	82	91	94	95

The conditions of the last experiment were adopted for general use and were tested over a wide range of protactinium concentrations and solution volumes.

(b) *Co-deposition on barium fluoride*—The enhancement of the co-deposition in the previous series of experiments by a large excess of barium suggested that the sparingly soluble barium fluoride might co-deposit protactinium as well as or better than the fluozirconate. The conditions were investigated over a wide range of protactinum concentrations and volumes of solution.

(i) Effect of quantity of added barium. Solutions were each made 2·5N in hydrofluoric acid.

Barium added, mg/ml	0·5	1·0	2·5	10
Per cent Pa carried down	42	57	69	>99

It was found that the co-deposition is even more favourable in less acid solution, and in ammonium fluoride solution is unaffected by the concentration of ammonium fluoride up to 10M. A further test of the necessary concentration of barium was made, using a solution that was 5M in ammonium fluoride but to which no free hydrofluoric acid had been added.

Barium added, mg/ml	0·5	0·9	1·8	4·3	8·2
Per cent Pa carried down	34	49	89	98	>99

The barium fluoride precipitated in this way is easily soluble in large amounts of cold water. The barium fluoride can be preferentially dissolved, thus further concentrating the protactinium; for instance, solution of 50 per cent of a precipitate in cold water dissolved less than 0·01 per cent of the protactinium.

5. *Solvent-extraction of the Protactinium*

(a) *Choice of solvent*—Most of the data to be reported refer to di*iso*propyl ketone, and indeed, this solvent remains the most suitable for the separation. However, during the investigation it ceased to be produced commercially, so a comparison was made with some alternative, more readily available, solvents. Equal volumes of solvent and aqueous phases were used in each experiment. The initial normality of the aqueous phase in hydrochloric acid and the percentage of Pa^{233} tracer found in the organic phase are given after each solvent.

Dichlorodiethyl ether, 6·0N, 13-30 per cent; amyl alcohol, 6·0N, 79 per cent; diethyl ketone, 6·0N, 87 per cent; mesityl oxide, 4·7N, 94 per cent; phorone, 6·0N, 90 per cent; methyl*iso*butyl ketone, 6·0N, 97 per cent; di*iso*propyl carbinol, 6·0N, 95·2 per cent; di*iso*propyl ketone, 6·0N, 99 per cent. The first of these solvents was only satisfactory in the presence of salting-out agents. Amyl alcohol, diethyl ketone, and mesityl oxide showed too great a mutual solubility with water. Phorone, which had to be used above its melting-point, 28°, was too liable to condensation reactions which were catalyzed by aluminium chloride.

To study the mutual miscibility and extraction of hydrochloric acid by the solvent, equal volumes of di*iso*propyl ketone and varying concentrations of hydrochloric acid were equilibrated by shaking together for twenty minutes in ampoules in a thermostat at 25°. The change in acidity was determined by titration of the aqueous phase.

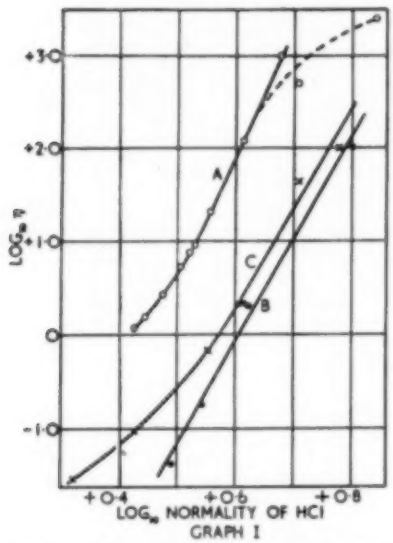
Initial normality of aqueous phase	3·12	3·47	4·16	6·26	8·00	9·76	12·00
Final normality of aqueous phase	3·08	3·46	4·10	6·25	7·80	9·20	9·20

Below 7N the volume change of the phases on equilibration is less than 2 per cent.

(b) *Conditions for the solvent extraction by di*isopropyl ketone—

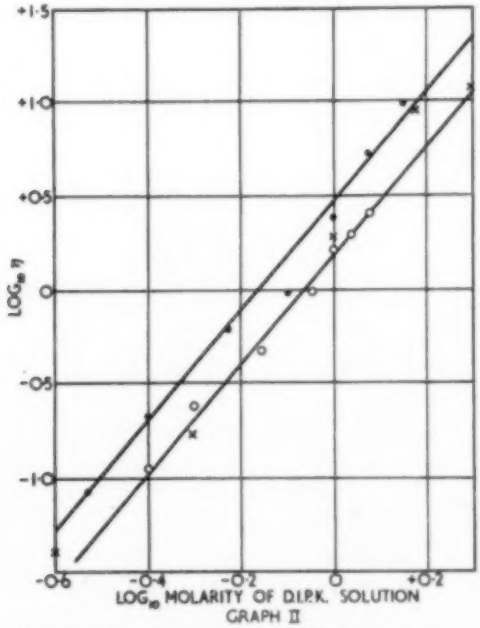
(i) Effect of acid concentration. 1-ml volumes of hydrochloric acid at various concentrations were equilibrated with equal aliquots of a solution of the chloride complex of protactinium in di*iso*propyl ketone at 18° in polythene capsules. Equilibrium was found to be established in less than five minutes. The results are presented in Graph I. Curve A refers to experiments with Pa^{231} at 0·02 mg/ml, and curve B refers to experiments with Pa^{233} at tracer concentrations, the latter experiments being conducted in glass vessels. The same data are presented in a different form in Graph V.

(ii) Effect of dilution of ketone with benzene. The extraction of protactinium from hydrochloric acid solutions between 3 and 8N by pure benzene was shown to be much less than 0·1 per cent. The variation of the extraction coefficient with the concentration of di*iso*propyl ketone in benzene was studied with an aqueous phase 6N in hydrochloric acid and with an initial concentration of Pa^{231} of about 0·04 mg/ml. 2-ml aliquots of each phase were equilibrated in each experiment. The results are presented in Graph II.



GRAPH I

GRAPH I.—Relation between the extraction coefficient for the protactinium and the concentration of hydrochloric acid in the aqueous phase. Curve A, Pa^{231}: 0·02 mg/ml. Curve B, Pa^{233}: tracer concentration (glass vessels). Curve C, Pa^{231}: 0·002 mg/ml in presence of aluminium fluoride complex.



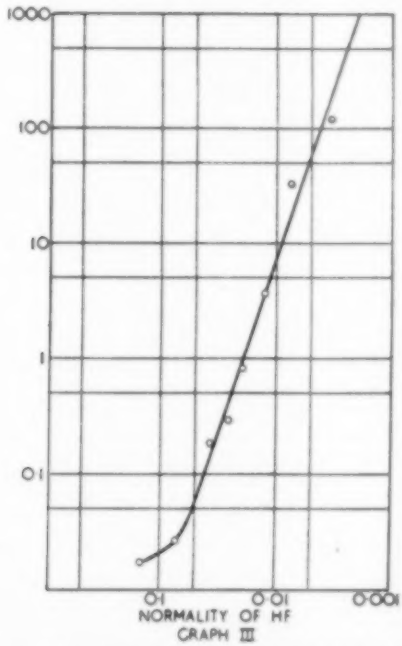
GRAPH II

GRAPH II.—Relation between the extraction coefficient for the protactinium and the concentration of ketone in the benzene phase.

× First experiment
○ Second experiment
● Third experiment

Two di*iso*propyl ketone purification cycles were carried out between the first and second, and second and third experiments.

(iii) Effect of fluoride on the extraction. The easiest method of returning the protactinium from the solvent to true solution in an aqueous phase was found to be extraction with aqueous hydrofluoric acid. The effect of the concentration of the hydrofluoric acid on the re-extraction was studied, using a solution of the chloride complex in di*iso*propyl ketone, prepared by extraction from 6N hydrochloric acid solution and re-extracting the organic phase with 7·4N hydrochloric acid containing varying concentrations of hydrofluoric acid. The experiments were conducted with Pa^{231} at a concentration of about 0·004 mg/ml, using 2 ml of each phase. The results are presented in Graph III.



GRAPH III.—Re-extraction of complex by 7·4N hydrochloric acid containing varying concentrations of hydrofluoric acid.

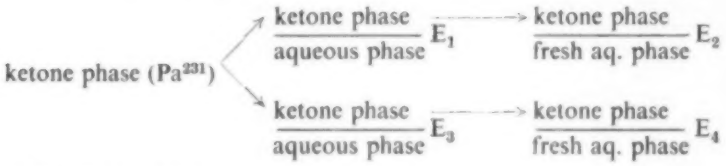
It was found that, if a strongly fluoride complexing ion was added to these fluoride extracts, it became possible again to solvent-extract the protactinium. Aluminium chloride was found convenient for this purpose. The ratio of the concentration of aluminium to fluoride ion necessary for solvent-extraction of the fluoride-containing solution was investigated. The experiments were made with an 8N hydrochloric acid solution, 0·6N in hydrofluoric acid and containing about 0·01 mg/ml of Pa^{231}. 3 ml of each phase were used and the aluminium added as anhydrous aluminium chloride.

Ratio Al/F	0·22	0·44	0·88	1·6
Per cent Pa^{231} extracted	2·0	4·3	88	100

The effect of the hydrochloric acid concentration on the solvent extraction from fluoride-complexed solution was studied with the aid of a solution with an aluminium to fluoride concentration ratio of 1·72 and a fluoride concentration of 0·51N. The

protactinium concentration was about 0·002 mg/ml, and 2 ml of each phase were used. The results are presented in curve C on Graph I.

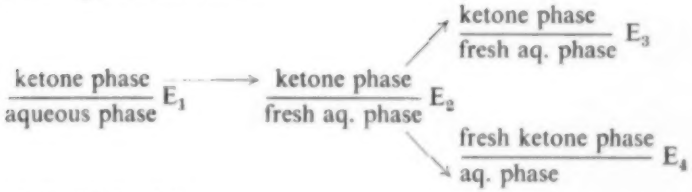
(iv) Homogeneity of protactinium solutions. Since the fraction of the protactinium extracted from an aqueous 6N hydrochloric acid solution was greater than that previously reported,[9] some repetitive solvent extractions were performed to determine if all the protactinium in the aqueous phase showed the same solvent-extraction behaviour. In each experiment the two phases were re-equilibrated with equal volumes of the protactinium-free opposite phase, and the distribution of the protactinium was redetermined. 7·0N. hydrochloric acid:


ketone phase (Pa231)
ketone phase / aqueous phase E1
ketone phase / fresh aq. phase E2
ketone phase / aqueous phase E3
ketone phase / fresh aq. phase E4

* $E_1 = 0{\cdot}041 \pm 0{\cdot}004$
$E_2 = 0{\cdot}038 \pm 0{\cdot}004$
$E_3 = 0{\cdot}068 \pm 0{\cdot}005$
$E_4 = 0{\cdot}037 \pm 0{\cdot}004$

* Percentages refer to aqueous phase.

2·80N hydrochloric acid:

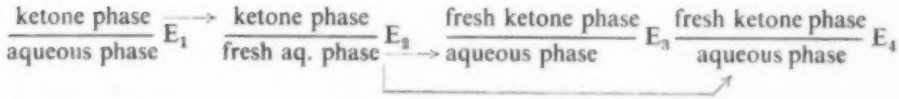

ketone phase / aqueous phase E1
ketone phase / fresh aq. phase E2
ketone phase / fresh aq. phase E3
fresh ketone phase / aq. phase E4

* $E_1 = 66{\cdot}2 \pm 0{\cdot}6$
$E_2 = 66{\cdot}7 \pm 0{\cdot}6$
$E_3 = 65{\cdot}3 \pm 0{\cdot}6$
$E_4 = 67{\cdot}1 \pm 0{\cdot}6$

* Percentages refer to solvent phase.

3·20N hydrochloric acid:

* $E_1 = 85{\cdot}0 \pm 0{\cdot}8$
$E_2 = 85{\cdot}1 \pm 0{\cdot}8$
$E_3 = 87{\cdot}9 \pm 0{\cdot}8$
$E_4 = 84{\cdot}8 \pm 0{\cdot}8$


ketone phase / aqueous phase E1
ketone phase / fresh aq. phase E2
fresh ketone phase / aqueous phase E3
fresh ketone phase / aqueous phase E4

In other experiments using solutions that probably contained hydrolyzed protactinium species, particularly for instance those obtained after inadequate solution of hydroxide precipitates, a part of the protactinium could not be extracted into solvent, and variable extractions between 60 and 90 per cent were obtained, even in 6N hydrochloric acid. Evidence was also obtained that colloidal silica was particularly effective in preventing the extraction of the protactinium. This was confirmed in some experiments in which the variation in the percentage extraction with the amount of added sodium silicate

was investigated. The aqueous phase was 6N hydrochloric acid and contained almost 0·004 mg/ml of Pa^{231}. 0·5 ml of each phase was used.

Sodium silicate added, mg/ml	20	2·1	1·5	0·8	0·2
Per cent Pa extracted	22	56	60	64	68·5

In the first four experiments the precipitated silica was visible.

(v) Effect of temperature. This influence of the temperature on the distribution of protactinium between a 2·90N hydrochloric acid solution and di*iso*propyl ketone was investigated, using 1 ml of each phase, and equilibrating the phases for ten minutes at the different temperatures. Since the effect proved to be very small, several measurements were made at each temperature. Only the mean and the standard deviation are recorded.

Per cent extraction	$72·1 \pm 0·6$	$72·1 \pm 0·7$	$72·3 \pm 0·6$	$70·6 \pm 0·7$
Temperature	0·7°	13·0°	18·3°	40°

During these experiments it was observed that the ketone solutions were especially unstable at elevated temperatures, and the protactinium adsorbs even on the polythene vessels. A comparison was made between the losses from the ketone solutions at 18°C and at 40°C.

			18°C		
Time	0	15 min	150 min	260 min	24 hr
Count on aliquot of solution	3420	3470	3440	2880	2641

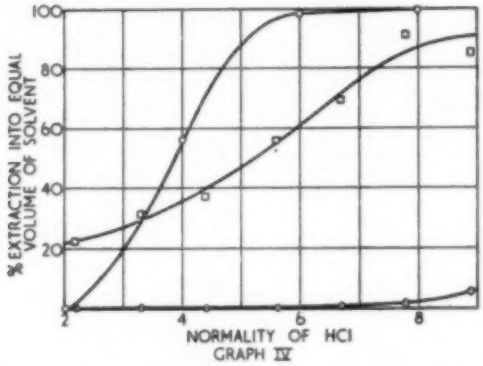
			40°C		
Time	0	10 min	35 min	50 min	65 min
Count on aliquot of solution	1750	1582	1333	1390	1190

For this reason the extractions at 40°C referred to above were calculated from the aqueous-phase content and the activity balance. All other experiments at room temperature were completed before adsorption occurred.

(c) *Separation from other elements*—The data above suggested the possibility of a cyclic solvent extraction process which should give a good separation from most elements. Various combinations of steps can be envisaged, and some of the factors involved are examined in the following typical process. The protactinium solution was made 7N in hydrochloric acid and 0·5N in hydrofluoric acid and extracted with solvent. The excellent separation of iron and polonium from the protactinium at this stage can be judged from Graph IV. The data displayed in this graph were obtained in control extractions using Po^{210} and macroscopic concentrations of iron, the latter element being estimated gravimetrically. The initial concentration of iron in the aqueous phase was about 5 mg/ml.

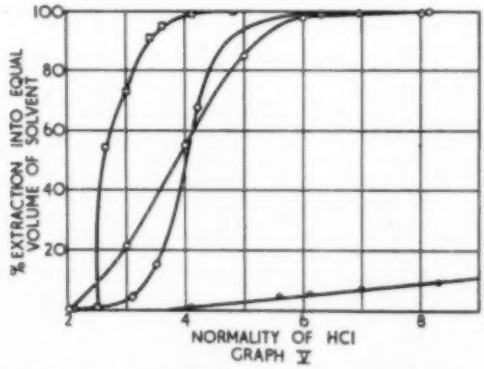
Naturally elements with insoluble fluorides, such as thorium, can be separated very efficiently at this stage. The data of STEVENSON and HICKS[13] show that more than 90 per cent of the tantalum would be extracted under these conditions, and less niobium. A rough estimate of the niobium gave 30 per cent extraction. About 50 per cent of stannic tin was extracted. Similar gravimetric experiments showed that ~7 per cent of Zr^{4+} and less than 2 per cent of UO_2^{2+}, Ti^{4+}, V^{5+}, or Mn^{2+} were extracted.

Only 0·4 per cent of the protactinium is extracted by each sweep with an equal volume of solvent from this aqueous phase, so that the extraction can be repeated two or three times without much loss of protactinium. The fluoride in the aqueous phase was then complexed with aluminium chloride and the solution re-extracted. The increase salt concentration increases the extraction of some elements, but even when the solution



GRAPH IV.—Percentage extraction as a function of the normality of hydrochloric acid in the aqueous phase. Hydrofluoric acid concentration constant at 0·5N.
○ Fe; □ Po^{210}; ◊ Pa^{233}.

was saturated with aluminium chloride, less than 1 per cent of the Th^{4+}, Al^{3+}, Ti^{4+}, V^{5+}, Mn^{2+}, and Ba^{2+} in the aqueous phase was extracted. However, the extraction of zirconium increased about threefold, and that of uranyl rose to 30 per cent. The protactinium passes almost entirely into the solvent phase, as shown in Graph I. The solvent phase containing the protactinium was then washed with 8N hydrochloric



GRAPH V.—Percentage extraction as a function of the normality of the fluoride-free acid phases.
□ Pa^{231}; ○ Fe; ◊ Pa^{233}; ● Zr.

acid. The distribution of protactinium, iron, and zirconium at various concentrations of hydrochloric acid were investigated. The iron and zirconium were estimated gravimetically. The results are shown in Graph V.

V^{5+}, Mn^{2+}, Al^{3+}, Mg^{2+}, and Cr^{3+} are retained less than 2 per cent by the solvent; titanium (Ti^{4+}) was about 3 per cent and tin (Sn^{4+}) about 65 per cent retained. More surprising, about 17 per cent of the cadmium in the aqueous phase passed into the

solvent from 6N acid, and 24 per cent from 8N acid. This hydrochloric acid wash therefore enhances the separation from uranyl and zirconium. The protactinium was finally extracted from the solvent phase by 0·5N hydrofluoric acid 8N in hydrochloric acid, and the purification cycle was repeated. The yield of the single cycle without repetition of any stage was better than 98 per cent.

(d) *Alternative methods of recovery from the solvent*—Besides hydrofluoric acid, various alternative aqueous reagents which re-extracted the protactinium from the solvent were examined. An ammonium fluoride solution containing 100 mg/ml of the salt extracted more than 98 per cent of the protactinium when one-thirtieth of the volume of the solvent was used. 100-volume hydrogen peroxide was nearly as effective. An ammonium thiocyanate solution (100 mg/ml) removed the protactinium, while leaving most of the iron in the solvent.

6. *Destruction of the Fluoride Complex*

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Although protactinium can be separated from its fluoride complex by the extraction process above, it was sometimes desirable to find a more direct process. Although the complex was found to be stable at pH ~9·0, it broke down in caustic soda solution and the protactinium could be completely separated on a hydroxide precipitate. It was observed that, provided this precipitate was not allowed to age, it could be dissolved in hydrochloric acid to give a solution displaying the normal extraction coefficient with di*iso*propyl ketone and therefore, presumably, free of colloidal material. Repeated evaporation of the fluoride complex with strong hydrochloric acid was also found to drive off the fluoride and produce a solution from which the protactinium could be completely extracted by the solvent.

7. *Examples of the Separation followed with Pa^{233} Tracer*

(a) *A heavy-metal sulphate precipitate*—This siliceous material consisted mainly of the sulphates of lead, barium, and calcium. Two methods of opening up were used. In the first, 1-gm samples were treated with 10 ml of 60 per cent oleum, and a known amount of Pa^{233} tracer added to the mixture. The lead, barium, and calcium sulphates were dissolved, and the siliceous residue, containing the protactinium, was separated and dissolved in 5 ml of 40 per cent hydrofluoric acid. Alternatively it was found that the original material could be attacked directly with 40 per cent hydrofluoric acid containing the Pa^{233} tracer, leaving the heavy-metal sulphates as residue and dissolving both Pa^{231} and Pa^{233}. Either solution was diluted to 100 ml and an excess of barium chloride solution added. The barium fluoride precipitate was washed until no obvious decrease in bulk took place. The remaining precipitate consisted presumably of fluosilicates and was dissolved in 1M aluminium nitrate solution, 6N in nitric acid. The protactinium was then carried down on a manganese dioxide precipitate, sufficient manganous chloride and potassium permanganate solutions to produce ~10 mg precipitate per ml of original solution being added, and the mixture digested at 100°C for half an hour. The resulting precipitate was separated, washed, and dissolved in 20 ml 7N hydrochloric acid with a trace of sodium nitrite. Alternatively the precipitate was leached with 10 ml of 1N hydrofluoric acid. In some analyses the manganese dioxide stage was omitted entirely, and the fluosilicate precipitate dissolved in 7N hydrochloric acid also 1M in aluminium chloride. The hydrofluoric acid leach from the manganese dioxide was also made 7N in hydrochloric acid and 1M in aluminium

chloride. The hydrochloric-acid solution from either of these three variations was then extracted with an equal volume of di*iso*propyl ketone, and the α-activity of the extract measured. The α-activity of this preparation was considerably reduced by ignition, since an appreciable fraction of the polonium follows the protactinium. However, separation from most of the polonium can be effected by re-extraction from the solvent into 7–8N hydrochloric acid, 0·5N in hydrofluoric acid. In the more extensive solvent cycles performed on the uranyl solution, complete separation from polonium was achieved. The yield calculated on Pa^{233}-recovery in this separation varied from 80–85 per cent, depending on the variation employed.

(b) *A uranyl solution*—The solution was made 8N in hydrochloric acid and 0·5N in hydrofluoric acid and the tracer Pa^{233} added. Direct extraction with di*iso*propyl ketone removed many impurities, e.g., iron and polonium. Extraction after adding aluminium chloride to complex the fluoride present brought the protactinium into the solvent layer. Washing this layer with 8N hydrochloric acid removed those elements whose extraction had been enhanced by the presence of aluminium chloride, e.g., uranium and zirconium. Finally the protactinium was back-extracted with 6-8N hydrochloric acid, 0·5N in hydrofluoric acid. The next solvent cycle avoided the use of aluminium chloride, repeated ammonia precipitation and hydrochloric acid solution, or continued evaporation with hydrochloric acid, being used to remove fluoride. In either case the efficiency of a cycle was 98 per cent or more, without repetition of any step. At the most two of these cycles were found to be sufficient to achieve radiochemical purity.

DISCUSSION

No evidence of volatility of protactinium from aqueous solutions has been found. The residues obtained after evaporation of aqueous solutions do not lose protactinium on ignition below 800°, and thus separation from polonium can easily be effected.

The results obtained in the barium fluoride co-deposition experiments suggest that a compound, presumably $BaPaF_7$, is very sparingly soluble. This has been confirmed by the preparation of a macroscopic amount of this compound. Its analysis and other properties will be described subsequently. SCHUMB, EVANS, and HASTINGS,[15] observation on the separation of barium sulphate from hydrofluoric acid solution containing sulphate ion when the protactinium content of the mixture remained in solution, suggests that the following salts are increasingly insoluble.

$$BaF_2,\ BaPaF_7,\ BaSO_4.$$

A disappointing feature of this investigation was the discovery that the ketonic solution of the protactinium chloride complex is not indefinitely stable, and slowly loses activity by adsorption on the walls even in polythene vessels. Various ketonic solvents can be used for this separation, but di*iso*propyl ketone seems to have the best combination of properties. The slope of Graph II showing the relation between the logarithm of the apparent coefficient of extraction and the molarity of ketone in benzene solution is almost exactly three. As has been shown by MCKAY and HEALY[16] (see also PEPPARD *et al.*[17]), the linear relation with the integral slope at low ketone concentration indicates that the protactinium is present in the solvent

[15] W. C. SCHUMB, R. D. EVANS, and J. L. HASTINGS, *J. Amer. Chem. Soc.*, **61**, 3453 (1939).
[16] H. A. C. MCKAY and T. V. HEALY, *Rec. Trav. chim.*, to be published.
[17] D. F. PEPPARD, J. P. FARIS, P. R. GRAY, G. W. MASON *J. Phys. Chem.*, **57**, 294 (1953).

as a complex containing three moles of ketone, for instance $PaCl_5 \cdot 3(C_3H_7^i)_2CO$. The linearity of Graph III, which also shows a slope of three, should facilitate identification of the fluoride complex or complexes, and a more detailed study of this subject is in progress. The re-equilibration experiments show that the extracting complex is formed, reversibly, by all the protactinium in the solution. The absence of a measurable temperature coefficient means that the heat of formation of the complex cannot be greater than ± 1 kilocal.

Only two examples of the combination of these processes into an analytical procedure have been given, because the most appropriate combination depends on the other components of the mixture. With small quantities of material it is often best to reverse the separation cycle, extracting from 6–8N hydrochloric acid and re-extracting the solvent with 6–8N hydrochloric acid 0·5N in hydrofluoric acid. This solution is then evaporated repeatedly with concentrated hydrochloric acid and a further cycle carried out. This avoids the use of aluminium salts for complexing the fluoride.

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ACKNOWLEDGEMENTS

This paper is published by permission of the Admiralty, one of us (J. G.) being with the Services Electronics Research Laboratory, Royal Naval Scientific Service. The generous assistance of U.K. Atomic Energy Authority personnel in connection with materials is also acknowledged. The authors are indebted to Miss B. J. COLGRAVE for assistance with the preparation and counting of samples.

J. Inorganic and Nuclear Chemistry, 1956, Vol. 2, pp. 60–65. Pergamon Press Ltd., London

STUDIES IN ALUMINIUM SOAPS—I

ALUMINIUM TRI-SOAPS

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(*Received* 27 *June* 1955)

Abstract—It has been found that three moles of isopropanol can be distilled out azeotropically when one mole of aluminium isopropoxide is treated with an excess of fatty acids in benzene. The products, on removal of the excess fatty acids by a suitable solvent such as dioxane or acetone, were in all cases found to be aluminium tri-soaps. Tri-valerate, tri-laurate, tri-myristate, tri-palmitate, and tri-stearate of aluminium have been prepared by this method. The tri-soaps are found to give quite mobile solutions in benzene. The failure of earlier workers to prepare tri-soaps of aluminium has been explained on the basis of the slowness of the final stage of the reaction caused by steric hindrance. It has been shown that there is an exothermic reaction between aluminium isopropoxide and acetic anhydride, but the reaction becomes slow towards the end. However, aluminium tri-acetate can be prepared by refluxing aluminium isopropoxide with an excess of acetic anhydride.

THE ALUMINIUM salts of higher fatty acids are articles of commerce used in several industries[1, 2, 3] and frequently employed in scientific investigations.[4, 5, 6] Their nature and composition are, however, surprisingly obscure. Commercially, these soaps are prepared by an aqueous double decomposition process, but in these products the fatty acid to aluminium ratio is generally lower than 2. A large amount of work has been done during the last two decades to prepare the tri-soaps of aluminium, but the general volume of evidence seems to indicate their probable non-existence.

MCBAIN and MCLATCHIE[7] studied the reaction between aluminium hydroxide and palmitic acid in 95 per cent and absolute methyl and ethyl alcohols, but got very hydrolyzed products. They also attempted the reaction between aluminium ethoxide and palmitic acid in benzene, but could not achieve a ratio higher than 2 for fatty acid : aluminium. Similar results in aqueous solutions were obtained by MARKOWICZ,[8] OSTWALD and RIEDEL,[9] and also by SMITH, POMEROY, MCGEE, and MYSELS.[10]

EIGENBERGER and co-worker[11, 12] have carried out a detailed examination of both the aqueous and non-aqueous precipitation methods, and have concluded that the primary product in both the cases contained only one-and-a-quarter fatty acid groups per aluminium atom.

GRAY and ALEXANDER[13] have recently carried out an extensive study of the reaction between aluminium secondary butoxide and various fatty acids. From the

(1) S. B. ELLIOT, *Alkaline Earth and Heavy Metal Soaps*. Reinhold Publishing Corporation, New York (1946).
(2) F. J. LICATA, *Metallic Soaps*. Metasap Chemical Company, New Jersey (1940).
(3) R. G. BOSSERT, *J. Chem. Education* **27**, 10 (1950).
(4) G. A. PARRY and A. J. TAYLOR, *Trans. Faraday Soc.* **46**, 305 (1950).
(5) W. H. BAUER, J. FISHER, F. A. SCOTT, and S. E. WIBERLAY, *J. Phys. Chem.* **59**, 30 (1955).
(6) D. EVANS and J. B. MATTHEWS, *J. Colloid Sci.* **9**, 60 (1955).
(7) J. W. MCBAIN and W. L. MCLATCHIE, *J. Amer. Chem. Soc.* **54**, 3266 (1932).
(8) E. MARKOWICZ, *Farben Ztg.* **34**, 326, 414, 503 (1928).
(9) WO. OSTWALD and R. RIEDEL, *Kolloid Z.* **69**, 185 (1934).
(10) G. H. SMITH, H. H. POMEROY, C. G. MCGEE, and K. J. MYSELS, *J. Amer. Chem. Soc.* **70**, 1053 (1948).
(11) E. EIGENBERGER, *Fette u. Seifen* **49**, 505 (1940).
(12) E. EIGENBERGER and A. EIGENBERGER-BITTNER, *Kolloid Z.* **91**, 287 (1940).
(13) V. R. GRAY and A. E. ALEXANDER, *J. Phys. Chem.* **53**, 23 (1949).

analyses of the products, as well as from the heats of reaction, they concluded that not more than two fatty acid groups combine per aluminium atom.

McGEE[14] has discussed the reasons for the failure to prepare tri-soaps by earlier workers. According to him, the tri-soap will have a structure such that aluminium would be at the centre of an octahedron and the oxygen atoms of the three carboxyl groups would occupy the six co-ordination positions. Such a molecule will have a solubility similar to that of the fatty acid, and hence it would be found with the free acid and not in the residue after treatment with solvents like dioxane and acetone.

Contrary to the evidence cited above, LAWRENCE[15] is of the opinion that aluminium tri-soaps do exist. According to him, aluminium alkoxides when heated with excess fatty acids evolve three moles of the corresponding alcohol which can be distilled out. GRAY and ALEXANDER (*loc. cit.*) have confirmed the above observation. However, according to them the full amount of alcohol is distilled out only at a high temperature when other side reactions cannot be ruled out. These workers have also analyzed the products after extraction with dioxane, and in no case were more than two fatty acid groups found to be combined per aluminium atom.

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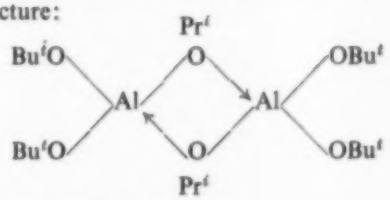
GLAZER, McROBERTS, and SCHULMAN[16] have described the preparation of aluminium tri-laurate by the reaction between aluminium tri-methyl and lauric acid in dry benzene. Although the analytical data are not very satisfactory, they have shown that the product did not give gels in hydrocarbon solvents. Due to the presence of a hydroxy group through which they can polymerize, the di-soaps of aluminium exhibit the characteristic property of giving highly viscous solutions or gels when dissolved in hydrocarbons.

In a recent communication,[17] it has been shown that aluminium tri-palmitate and tri-stearate can be prepared by the following reaction:

$$Al(OPr^i)_3 + 3RCOOH \rightarrow Al(OOCR)_3 + 3Pr^iOH$$

if the isopropanol is continuously fractionated out azeotropically with benzene. In the present investigation, the above method of preparation has been successfully extended to the preparation of aluminium tri-valerate, tri-laurate, and tri-myristate also. It has been found that per mole of the isopropoxide, two moles of the isopropyl alcohol are evolved out quite rapidly, but the replacement of the third isopropoxy group is very slow. Similar observations have been recorded when aluminium isopropoxide reacts with various alcohols[18, 19] and tertiary butyl acetate.[20] From molecular weight measurements, it was shown that mono-isopropoxy di-tertiary butoxide of aluminium is a dimer in benzene, and hence, it could be assigned the following probable structure:



[14] C. G. McGEE, *J. Amer. Chem. Soc.* **71**, 278 (1949).
[15] A. S. C. LAWRENCE, *J. Inst. Petroleum* **31**, 303 (1945).
[16] J. S. GLAZER, T. S. McROBERTS, and J. H. SCHULMAN, *J. Chem. Soc.*, 2082 (1950).
[17] R. C. MEHROTRA, *Nature* **172**, 74 (1953).
[18] R. C. MEHROTRA, *J. Ind. Chem. Soc.* **30**, 585 (1953).
[19] R. C. MEHROTRA, *J. Ind. Chem. Soc.* **31**, 85 (1954).
[20] R. H. BAKER, *J. Amer. Chem. Soc.* **60**, 2673 (1938).

It can be expected on steric considerations that further reaction, particularly with ramified molecules, will be slow. Similar observations have been made in the attempts to prepare zirconium tetra-tertiary butoxide from zirconium methoxide and ethoxide.[21, 22, 23] The thermochemical as well as the preparative results of GRAY and ALEXANDER (*loc. cit.*) and also earlier workers can be easily understood on the basis of the above simple explanation.

In order to establish definitely that the tri-soaps are true molecular entities and not merely mixtures of the di-soaps with an equimolecular quantity of the free fatty acid, the tri-soaps prepared by the reaction between aluminium isopropoxide and fatty acid (molar ratio = 1 : 3) have been treated with solvents like ethyl acetate, acetone, and dioxane, in which the fatty acids are readily soluble and the tri-soaps are comparatively insoluble. Further, the reaction of aluminium iso-propoxide with an excess of fatty acid has been carried out. In all cases, it has been found that, even under extremely dry conditions, three moles of isopropanol can be distilled out per mole of aluminium isopropoxide employed. The excess fatty acid was removed in the case of valeric acid by heating the product to a much higher temperature than the boiling-point of valeric acid under reduced pressure. In the case of higher fatty acids, the treatment with suitable solvents like ethyl acetate, acetone, and dioxane has been resorted to. In partial confirmation of the prediction of MCGEE (*loc. cit.*), it has been found that aluminium tri-valerate, tri-laurate, and tri-myristate exhibit an appreciable solubility to give mobile solutions in boiling dioxane, but the soaps separate out again on cooling the solution. The solubility of the palmitate and stearate soaps appears to be very low in dioxane, but all the soaps give mobile solutions in benzene. These observations are of interest, as they confirm the views of MCROBERTS and SCHULMAN[24] regarding the gelation of aluminium soaps in hydrocarbons.

The lowest member of the series, a simple substance like aluminium tri-acetate, does not appear to have been isolated with definiteness. It was first attempted to prepare the tri-acetate by the reaction between aluminium isopropoxide and a slight excess of acetic anhydride in benzene:

$$Al(OPr^i)_3 + 3(CH_3CO)_2O \rightarrow Al(CH_3COO)_3 + 3CH_3COOPr^i.$$

However, the reaction appeared to be slow towards the end, and even after the mixture had been refluxed for four to five hours the product was not pure aluminium tri-acetate, but was contaminated with aluminium mono-isopropoxide diacetate. It has been possible to prepare aluminium tri-acetate by the reaction between aluminium isopropoxide and excess acetic anhydride. A comparison of the above two products was interesting; the tri-acetate immediately goes into solution in cold water, but the mono-isopropoxy diacetate is not wetted easily by hot water or even by hot caustic soda solution. Both are insoluble in benzene.

EXPERIMENTAL

Apparatus. All-glass apparatus with standard interchangeable joints was used, and careful special precautions were taken to exclude moisture. All fractionations were carried out in a column packed with Raschig rings and fitted to a total-condensation variable take-off stillhead.

[21] D. C. BRADLEY, R. C. MEHROTRA, and W. WARDLAW, *J. Chem. Soc.*, 4204 (1952).
[22] R. C. MEHROTRA, *J. Amer. Chem. Soc.* **76**, 2266 (1954).
[23] R. C. MEHROTRA, *J. Ind. Chem. Soc.* **31**, 904 (1954).
[24] T. S. MCROBERTS and J. H. SCHULMAN, *Proc. Roy. Soc.* **A200**, 136 (1950).

Materials. Aluminium isopropoxide was prepared as described by YOUNG, HARTUNG, and CROSSLEY,[25] and the product was distilled at 106°/1·5 mm. On analysis, the sample gave Al 13·22, and *iso*-PrO 87·0 per cent.

The fatty acids—valeric, lauric, myristic, palmitic, and stearic—were reagent grade products of B.D.H. or Kahlbaum. They were purified by repeated crystallization and finally fractionated under reduced pressure.

Acetic anhydride was a Merck (extra pure) product, and was carefully fractionated over a column before use.

Benzene and acetone were B.D.H. Analar products. Benzene was dried by storage and careful fractionation over metallic sodium. Acetone was kept over anhydrous K_2CO_3 overnight, decanted off, and distilled. The distillate was again kept overnight over anhydrous magnesium sulphate and then distilled after decantation. The distillate was finally refluxed over some $Al(OPr^i)_3$ and then fractionated carefully over a column.

Ethyl acetate and dioxane were B.D.H. (technical) products. Ethyl acetate was dried over anhydrous K_2CO_3 and purified by fractionation. Dioxane was treated and purified according to VOGEL.[26]

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In view of the extreme susceptibility of the materials to hydrolysis, the solvents were always freshly distilled direct into the reaction mixture.

Analytical Methods. Aluminium was determined gravimetrically as the oxide by the direct ignition of the soaps in the case of higher fatty acids, and as oxinate in the case of lower ones. Carbon and hydrogen determinations have been carried out by WEILER and STRAUSS (Oxford). The alcohol content in the benzene-alcohol azeotrope was determined by an oxidimetric method[27] which could be applied directly, as benzene was found not to reduce potassium dichromate at the room temperature.

Preparation of Aluminium Tri-soaps. The general method of preparation is the same for the soaps of all the fatty acids, and hence details will be given in the case of one soap, aluminium tri-palmitate, only.

Aluminium Tri-palmitate. To a mixture of aluminium isopropoxide (4·25 g) and palmitic acid (redistilled at 100°/1 mm, 16·03 g; molar ratio of palmitic acid: aluminium isopropoxide = 3 : 1) was distilled extra dry benzene (about 90 cc). The mixture was refluxed under a column at a bath temperature of 150–160°. About 20 cc of the distillate were collected slowly between 71–74° in the course of about an hour, and was found to contain 2·4 g of isopropanol. The reaction became slow at this stage. The temperature of the distilling liquid rose to 80° and fell to about 78° in the course of about half an hour. As soon as a few drops of the distillate were collected, the temperature again rose to 80°. About 30 cc of the distillate were collected during six hours in this manner, and were found to contain 1·2 g of isopropanol. Refluxing was continued for another two hours, and the distillate was collected at 80° under a high reflux ratio (1 : 20). The product was present in the form of a mobile solution in the remaining benzene. This benzene was removed by distillation under reduced pressure, and the product (a slightly pale yellow solid) was heated at about 200° under 0·1 mm pressure for half an hour. The sample softened at about 75°, but became a clear liquid sharply at 98°. Total amount of isopropanol found in the distillate was

[25] W. G. YOUNG, W. H. HARTUNG, and F. S. CROSSLEY, *J. Amer. Chem. Soc.* **58**, 100 (1936).
[26] A. I. VOGEL, *Practical Organic Chemistry*, p. 175, Longmans, Green and Co., London, 1948.
[27] D. C. BRADLEY and W. WARDLAW, *J. Chem. Soc.*, 3450 (1950).

3·6 g, against 3·7 g required theoretically. The product on analysis gave Al 3·42, C 72·64, H 11·90 per cent. *Al(palmitate)*$_3$ requires Al 3·40, C 72·68, H 11·81 per cent.

Approximately 0·7 g of the soap was taken in dry acetone (30 cc), and the mixture refluxed for about fifteen minutes, after which the soap appeared to be unaffected. After cooling, the soap was filtered and the residue was dried under reduced pressure, leaving 0·7 g of a pale yellow powder. On analysis, it gave Al 3·44 per cent; m.p. 93–96°.

Another portion (about 1 g) of the soap was refluxed with dioxane (15 cc) for about fifteen minutes. The soap floated on the surface of the liquid, and melted. The dioxane appeared to penetrate inside the melted mass and cause swelling. After cooling, the insoluble soap was filtered and the residue heated under reduced pressure to about 100°. On analysis, it was found to contain 3·46 per cent Al; m.p. 95–96°. Melting-point of a mixture of the original soap and the sample after treatment with dioxane was found to be 95–96°, thus establishing their identical nature.

Another sample of the above soap was prepared, employing 1·81 g of aluminium isopropoxide and 10 g of palmitic acid (molar ratio of acid to aluminium = 4·5 : 1) in 70 cc benzene. The azeotrope collected between 72–80° during three hours was found to contain 1·6 g of isopropanol (theory, 1·6 g). The remaining benzene was removed under reduced pressure, giving a pale yellow powder. The sample (about 3 g) was refluxed with ethyl acetate (50 cc). The soap appeared to melt and stick to the walls of the flask. On cooling, a pale yellow powder separated out which was filtered and dried under reduced pressure (found, Al 3·50 per cent).

Aluminium Tri-stearate. Aluminium isopropoxide (1·51 g) and stearic acid (6·30 g; molar ratio 1 : 3) in benzene (80 cc) gave on refluxing under column a distillate (about 24 g) between 72–80° containing 1·25 g of isopropanol (theory, 1·32 g). The remaining benzene was removed under a high reflux ratio and finally under reduced pressure, yielding a white solid which was kept at 200–220° under 0·2-mm pressure for one hour. The solid softened at about 100°, and melted sharply to a clear liquid at 120°. (Found: Al 3·09, C 74·13, H 12·02 per cent. *Al(stearate)*$_3$ requires Al 3·07, C 73·92, H 12·07 per cent).

The above preparation was repeated after taking a slight excess of stearic acid (3·5 moles). 1·5 g of the product (a white powder) was refluxed with 20 cc of dioxane for fifteen minutes, and the insoluble residue after heating to 100° under reduced pressure was found to contain 3·26 per cent Al. On repeating the treatment with dioxane, the product was found to contain 3·32 per cent Al. Another portion of the original product was treated with acetone, and the insoluble residue on analysis gave 3·25 per cent Al.

Aluminium Myristate. Aluminium isopropoxide (1·45 g) and myristic acid (5·7 g; molar ratio 1 : 3·6) were allowed to react in benzene (60 cc) as usual. The product (slightly yellow powder) was refluxed with dioxane. A portion of the soap appeared to dissolve in dioxane and separated out on cooling. The insoluble mass gave on analysis 3·97 per cent Al. *Al(myristate)*$_3$ requires Al 3·81 per cent.

Aluminium Tri-laurate. Aluminium isopropoxide (1·5 g) and lauric acid (6·6 g; molar ratio = 1 : 4·5) were refluxed as usual in benzene (40 cc). The azeotrope collected between 72–80° was found to contain 1·26 g of isopropanol (theoretical amount 1·31 g). About 1·5 g of the product (a white powder) was refluxed in dioxane (20 cc), and appeared to give a clear mobile solution, from which the soap

separated out on cooling. Analysis of the separated mass after usual treatment gave 4·37 per cent Al. *Al(laurate)*$_3$ requires 4·32 per cent Al.

Another portion of the original product was treated with boiling acetone; it did not show any tendency to dissolve in acetone. The insoluble white powder after usual treatment was found to contain 4·46 per cent Al.

Aluminium Tri-valerate. Aluminium isopropoxide (3·46 g) and valeric acid (7·6 g; molar ratio = 1 : 4·4) were allowed to reflux in benzene (70 cc). The azeotrope collected between 71–80° was found to contain 3·0 g of isopropanol (theoretical amount, 3·04 g). The product (a white powder) was heated to 220° under 0·01-mm pressure and kept at this temperature for three hours. The white powder did not show any tendency towards melting. (Found: Al 8·20, C 54·46, H 8·24 per cent. *Al(valerate)*$_3$ requires Al 8·18, C 54·54, H 8·18 per cent.)

Another sample of the above soap was prepared by treating aluminium isopropoxide (4·4 g) and valeric acid (9·4 g; molar ratio 1 : 4·3) in benzene (70 cc). The product was treated with dioxane (150 cc), and a portion of the soap appeared to dissolve slowly. After cooling and filtering the residue, the product was dried as usual and was found to contain 8·21 per cent Al. To test the solubility of the soap in dioxane, a sample of the above product (0·5 g) was refluxed in dry dioxane (15 cc), and the soap dissolved very slowly to give a mobile solution from which the soap again separated out on cooling.

Reaction of Aluminium Isopropoxide with Acetic Anhydride in the Presence of Benzene. Acetic anhydride (3·4 g) was distilled dropwise in a solution of aluminium isopropoxide (1·93 g; molar ratio of acetic anhydride to aluminium = 3·3 : 1) in benzene (20 cc). A large amount of heat was evolved and the solution became viscous. The mixture was refluxed for nearly four hours at bath temperature of 100–110°, when a white precipitate gradually settled down. The supernatant liquid was decanted off and was found to contain very little aluminium. The residue was kept at 40° under reduced pressure for about one hour, giving a white mass. When the mass was added to water, a major portion appeared to dissolve readily, while a small portion remained floating on the surface and was water-repellent. On analysis, the product was found to contain Al 13·51, Pr^iO 6·1 per cent. A mixture of $Al(OAc)_3$ and $Al(OPr^i)(OAc)_2$ in the molar ratio of 3·75 : 1 requires Al 13·24, Pr^iO 6·1 per cent.

Preparation of Aluminium Tri-acetate by Reaction Between Aluminium Isopropoxide and Acetic Anhydride (excess). Acetic anhydride (about 20 cc) was distilled dropwise to solid aluminium isopropoxide (4·3 g). A large amount of heat was evolved, and, when the reaction mixture was refluxed for five hours at a bath temperature of 150–160°, a white powder gradually settled down. The supernatant liquid was decanted off and the residue was dried by heating to 100–110° under reduced pressure. The white solid was readily soluble in water, and gave, on analysis, Al 13·50, acetate 85·5 per cent. A portion of the white solid was refluxed for fifteen minutes with dioxane; it appeared to be unaffected. After filtering, the residue was again heated to 100° under reduced pressure, giving a white powder readily soluble in water. (Found: Al 13·50, acetate 86·6 per cent. *Al(acetate)*$_3$ requires Al 13·24, acetate 86·74 per cent).

ACKNOWLEDGEMENT

One of us (K. C. P.) is grateful to the Scientific Research Committee, U.P., for a scholarship, during the tenure of which a portion of the above work was carried out.

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J. Inorganic and Nuclear Chemistry, 1956, Vol. 2, pp. 66–68. Pergamon Press Ltd., London

A NEW ELUANT FOR THE SEPARATION OF THE ACTINIDE ELEMENTS

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(*Received* 17 *May* 1955)

SEVERAL groups have described the use of ammonium lactate solutions as the eluting agent for the separation of the actinide and the lanthanide elements from cation resin columns.[1–5] A new eluant, ammonium α-hydroxy-isobutyrate, has given much better separations than ammonium lactate for both of these groups of elements. This eluting agent was used in the recent separation and identification of mendelevium, element 101.[6] A typical elution curve for the actinide elements is shown in Fig. 1.

The experimental conditions are identical to those reported by this laboratory for the use of ammonium lactate.[4] A curve of pH *vs* elution peak position drop number for a 0·4 *M* ammonium α-hydroxy-isobutyrate solution with a 5 cm × 2 mm. Dowex-50 X-12 cation resin column operated at 87°C is shown in Fig. 2. Table 1 is a

TABLE 1

Element	Eluant Anion		
	Glycoleate	Lactate	α-Hydroxy-isobutyrate
$_{101}$Mv	—	—	0·05
$_{100}$Fm*	—	0·23	0·07
$_{99}$E†	—	0·33	0·13
$_{98}$Cf	0·60	0·41	0·20
$_{97}$Bk	0·70	0·65	0·45
$_{96}$Cm	1·00	1·00	1·00
$_{95}$Am	1·14	1·21	1·45

* Fermium. † Einsteinium.

comparison of ammonium glycoleate, ammonium lactate, and ammonium α-hydroxy-isobutyrate, in which elution peak positions are expressed relative to curium by a separation factor, α, with the free-column volume subtracted from all peak positions. Elutions of lanthanide tracers showed that the separations relative to gadolinium are

[1] W. E. NERVIK, private communication reported by D. C. DUNLAVEY and G. T. SEABORG, *Phys. Rev.*, **92**, 206 (1953).
[2] S. W. MAYER and E. C. FREILING, *J. Amer. Chem. Soc.*, **75**, 5647 (1953).
[3] L. WISH, E. C. FREILING, and L. R. BUNNEY, *J. Amer. Chem. Soc.*, **76**, 3444 (1954).
[4] S. G. THOMPSON, B. G. HARVEY, G. R. CHOPPIN, and G. T. SEABORG, *J. Amer. Chem. Soc.*, **76**, 6229 (1954).
[5] R. A. GLASS, *J. Amer. Chem. Soc.*, **77**, 807 (1955).
[6] A. GHIORSO, B. G. HARVEY, G. R. CHOPPIN, S. G. THOMPSON, and G. T. SEABORG *Phys. Rev.*, **98**, 1518 (1955).

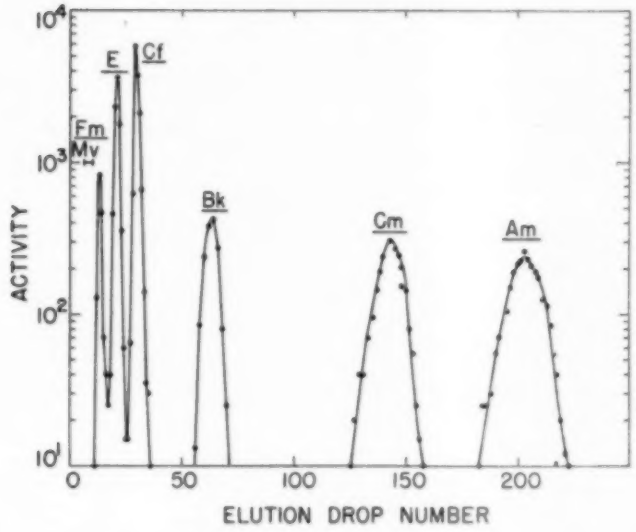

FIG. 1.—Elution of tripositive actinides from Dowex-50 with ammonium α-hydroxy-isobutyrate.

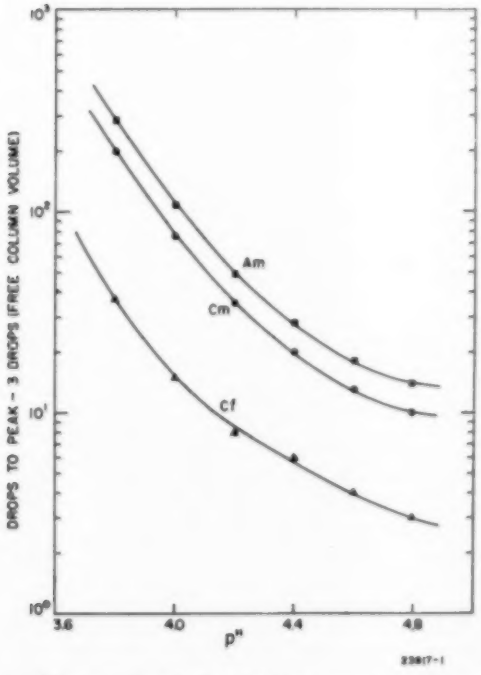

FIG. 2.—Elution peak positions versus pH of eluant.

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approximately the same as those for the analogous actinides relative to curium. This is the same behaviour as that exhibited by ammonium lactate, ammonium citrate, and similar eluants.*

The improvement in separations attendant to the replacement of a hydrogen by a methyl group on the alpha carbon is evident. A more complete investigation of these and similar complexing agents is in progress.

ACKNOWLEDGEMENTS

The assistance of MARGARET NERVIK and ROBERTA GARRETT in the column runs is gratefully acknowledged.

This work was performed under the auspices of the U.S. Atomic Energy Commission.

* We are grateful to Dr. E. C. FREILING for pointing out that our earlier report (reference 4) on ammonium lactate may have been misleading on the positions of the lanthanides and the actinides relative to each other. With ammonium α-hydroxy-isobutyrate as with ammonium lactate, promethium and americium elute approximately together.

J. Inorganic and Nuclear Chemistry, 1956, Vol. 2, pp. 69–78. Pergamon Press Ltd., London

NEW SHORT-LIVED ISOTOPES OF TIN FOUND IN FISSION*

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(*Received* 9 *June* 1955; *in final form* 28 *September* 1955)

Abstract—A radiochemical method for rapid (45 seconds) separation of tin from fission mixtures has been developed. Tin was separated by extraction of the stannous dithizonate complex into carbon tetrachloride from a tartrate solution adjusted to pH 8·5–9·0. The antimony daughters growing in were subsequently isolated by shaking the carbon tetrachloride phase with buffered tartrate solution.

Using this procedure, the following new neutron-rich isotopes of tin have been found: 2·6 ± 0·3-min Sn^{130}, 3·4 ± 0·5-min Sn^{131}, and 2·2 ± 0·3-min Sn^{132}. Improved half-lives are given for Sb^{130} (10·0 ± 0·5 min) and Sb^{132} (2·0 ± 0·2 min). These values have been used to correct previously measured fission yields for the corresponding antimony daughters. The corrected yields are for—10·0-min Sb^{130}, 2·0 ± 0·5 per cent; 23·1-min Sb^{131}, 2·5$_6$ ± 0·2 per cent; and for 2·0-min Sb^{132}, ~3 per cent.

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INTRODUCTION

THE problem of heavier tin isotopes, and in particular the question of tin-132, has attracted some attention in recent years as a result of developments in our knowledge of the origin of fission-yield fine structure. Several workers[1–5] have concluded from experimental and theoretical studies that the formation of fission fragments having closed shells of 50 protons or 82 neutrons must be especially favoured in the fission act itself. It thus becomes of major interest to find and characterize the heavy isotopes of tin ($Z = 50$) and if possible measure their fission yields. Especially interesting in this connection is tin-132, with closed shells of both 50 protons and 82 neutrons.

Only a very few nuclei with closed major shells of both protons and neutrons exist; the other such nuclei are the stable $_{20}Ca^{40}_{20}$, $_{20}Ca^{48}_{28}$, and $_{82}Pb^{208}_{126}$, and some of the very light nuclei. Such a nuclide as tin-132, with eight neutrons more than its heaviest stable isotope, might nevertheless be expected to exhibit unusual stability and have a measurably long half-life, because of the effect of the closed shells on the nuclear energy surface.[6] The effect of the $N = 82$ closed shell is that neutrons just before the closing of the shell are especially tightly bound, and that

* This work has been supported by the Royal Norwegian Council for Scientific and Industrial Research.
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(1) D. R. WILES (October 1950) M.Sc. Thesis in Chemistry, McMaster University, Hamilton, Canada (unpublished); see also D. R. WILES, B. W. SMITH, R. J. HORSLEY, and H. G. THODE (1953) *Canad. J. Phys.*, **31**, 419.
(2) L. E. GLENDENIN, E. P. STEINBERG, M. G. INGHRAM, and D. C. HESS (1951) *Phys. Rev.*, **84**, 860.
(3) A. C. PAPPAS (September 1953) Laboratory for Nuclear Science, Technical Report No. 63, Massachusetts Institute of Technology; see also A. C. PAPPAS (1954) *Z. Elektrochemie*, **58**, 620.
(4) D. R. WILES and C. D. CORYELL (1954) *Phys. Rev.*, **96**, 696; see also D. R. WILES (1954) *Z. Elektrochemie*, **58**, 623.
(5) P. FONG (1953) Ph.D. Thesis in Physics, University of Chicago (unpublished).
(6) C. D. CORYELL (1953) *Ann. Rev. Nucl. Sci.*, **2**, 305.

of the $Z = 50$ closed shell is that additional protons are less tightly bound. Thus, the result would be a lowering of the total decay energy, and a consequent increase in the length of the expected half-life. In this connection it should be mentioned that this also finds support in work by DUCKWORTH,[7] who finds unusually low mass (i.e., greater stability) for stable double-closed-shell nuclei, one of whose closed shells is only a subshell (e.g., $_{58}Ce_{82}^{140}$). The effect, amounting to about 3 MeV in the case of the $N = 82$ shell and the $Z = 58$ subshell, would be expected to be even larger for tin-132.

With the parameters of CORYELL, BRIGHTSEN, and PAPPAS,[8] the total decay energy (ground-state to ground-state) of tin-132 is calculated to be $3{\cdot}8 \pm 0{\cdot}6$ MeV. On this basis, and assuming $4{\cdot}0 \leq \log(\text{ft}) \leq 6{\cdot}0$ (allowed transition), one can estimate the half-life of tin-132 at between about two seconds and two minutes, by using the charts of comparative lifetimes given by MOSZKOWSKI.[9] It is, however, quite possible that the transition to the ground-state of antimony-132 is forbidden. This would result in a longer half-life than that estimated. Similarly, one would expect that tin-130 and tin-131 would have appreciable lifetimes. It thus seemed feasible to make a search for tin-132 and for other short-lived tin isotopes, and this is the aim of the present paper. Tin-133, on the other hand, has its last (83rd) neutron just outside the closed shell, and thus loosely bound. Its decay energy will be correspondingly higher, and its half-life must be very short indeed.

TABLE 1.—ISOTOPES OF ANTIMONY AND TELLURIUM IN THE MASS RANGE 127–133

	(22 per cent)	Te^{127m}	90 d
Sb^{127}	93 h → (78 per cent)	Te^{127}	9·3 h
		Te^{128}	stable
	(36 per cent)	Te^{129m}	33·3 ± 0·1 d
Sb^{129}	4·6 ± 0·1 h → (64 per cent)	Te^{129}	70 min
Sb^{130}*	12 ± 2 min ——————→	Te^{130}	stable
	(15 per cent)	Te^{131m}	30 h
Sb^{131}	23·1 ± 2 min → (85 per cent)	Te^{131}	25 min
Sb^{132}	1·9 ± 0·2 min ——————→	Te^{132}	77·7 ± 0·5 h
	(92 per cent)	Te^{133m}	63 ± 2 min
Sb^{133}	4·1 ± 0·3 min → (8 per cent)	Te^{133}	~2 min
Sb	40–70 min†		

* Mass assignment based on fission-yield measurements.[12]

† 40 min[11], 1·2 h[13], 1 h[14]. *Mass assignment:* 128, uncertain, based on fission-yield measurements;[12] 130, based on change in yield in going from thermal to 14 MeV neutron fission.[11]

[7] H. E. DUCKWORTH, C. L. KEGLEY, J. M. OLSON, and G. S. STANFORD (1951) *Phys. Rev.*, **83**, 1114.
[8] C. D. CORYELL, R. A. BRIGHTSEN, and A. C. PAPPAS (1952) *Phys. Rev.*, **85**, 732, see ref. 6.
[9] S. A. MOSZKOWSKI (1951) *Phys. Rev.*, **82**, 35.

Of the tin isotopes formed in fission, those of masses up to and including 127 are well known.[10, 11] From fission-yield studies of antimony isotopes, PAPPAS[12] found indications that tin-129 and tin-131 have half-lives of the order of five minutes.

The isotopes of antimony and tellurium in the mass-region of interest are, fortunately, fairly well known. The work of BARNES and FREEDMAN,[11] COOK,[13] and PAPPAS[12] gives the following picture of these nuclides (Table 1). Unless otherwise stated, the mass assignments are based on identification of known daughter and/or granddaughter activities.[12, 13]

EXPERIMENTAL METHODS

The thermal-neutron fission yields of tin isotopes with mass lower than 129 are expected to decrease very rapidly with decreasing mass number. At the same time, the half-life will increase with decreasing mass number. One would therefore expect to obtain significant quantities of only those isotopes which are above mass 129 in a one-minute thermal-neutron irradiation of uranium—all previously unknown. These would have radioactive antimony daughters, decaying in turn to give isotopes of tellurium and iodine.

On this basis it might be anticipated that as many as four activities with half-lives of less than five minutes could be present in the tin sample. As three of these are at present unknown, direct analysis of the tin decay-curve would be virtually impossible, even with the help of energy-selection counting.

Since the antimony and tellurium decay products of tin isotopes in question are fairly well known (cf. Table 1), application of the daughter-milking technique offers a fairly straightforward solution to the problem. Application of this technique requires a chemical separation method enabling the isolation of the element under study in the form of a stock solution, and the separation of the daughter element from this stock solution at convenient regular intervals. The decay-curve of the daughter activities must, of course, be unambiguously analysable.

It was thus decided to attack the problem by the following methods:

1. To separate tin from neutron-irradiated uranium as quickly as possible, and from the total tin solution to milk antimony at intervals of 2·0 min (1·5 min, 3·0 min, and other intervals were used). As indicated in the previous discussion, this was expected to give a sample of antimony presumably containing isotopes from mass 128 or 129 up to 132, and their tellurium and iodine decay products. The analysis of the decay-curves, whilst complex and tedious, should be possible with a fair degree of reliability.

2. To separate tin from equal portions of neutron-irradiated uranium at intervals of 2 min, and after a few hours to separate tellurium from these preparations and measure its activity. This tellurium could be expected to contain 33·5-d Te^{129}, 30-h Te^{131m}, and 77·7-h Te^{132}. This decay-curve would be quite easy to analyse, the main question being whether sufficient activity could be obtained of these longer-lived species. The method could be simplified further by separating tellurium first after about 30 min, and reprecipitating it after some hours, at which time it would contain nearly pure 77·7-h Te^{132}.

This second method was found to give very unreliable results, because of too low activities, and because of what appeared to be a slow exchange of carrier tin with the active species. As the antimony milking was found to work quite satisfactorily, this method was abandoned.

RAPID CHEMICAL SEPARATIONS

The standard methods for separating tin from fission mixture[15, 16] involve several sulphide precipitations and oxidation-reduction cycles. Specific scavenging steps are also necessary in most cases. Although this is a satisfactory method of separation in cases where time is not an important

[10] C. M. NELSON, B. H. KETELLE, and G. E. BOYD (November 1950) American Report ORNL 828.
[11] J. W. BARNES and A. J. FREEDMAN (1951) *Phys. Rev.*, **84**, 365.
[12] A. C. PAPPAS, Reference 3, pp. 56–72.
[13] G. B. COOK (June 1951) British Report AERE C/R-729.
[14] G. FORD, J. S. GILMORE, and R. W. SPENCE (October 1950) Personal Communication.
[15] J. A. SEILER (1951) Paper 269 in *Radiochemical Studies: The Fission Products*, C. D. CORYELL and N. SUGARMAN, Editors, NNES Div. IV, **9**, McGraw-Hill, New York.
[16] W. W. MEINKE (March 1952) American Report AECD-3084.

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consideration, it is a very long and tedious procedure. The study of shorter-lived tin isotopes has thus been seriously limited by the lack of a rapid separation method.

The fast separation method used in the present study is based on the extraction of the stannous dithizonate into carbon tetrachloride from a slightly basic solution.[17] From a tartrate solution adjusted to pH 8·5–9·0, only palladium, cadmium, indium, and tin among the fission products are extracted as dithizonates. From a consideration based on the yield-mass curve and the charge distribution in thermal-neutron fission of uranium,[2] it can be shown that the fission yields of palladium, cadmium, and indium are much lower (by a factor of about 100) than the yields of the tin isotopes of interest. It was thus assumed that these contaminants did not interfere in the present work. Since, moreover, none of these contaminants is back-extracted along with the antimony, they were found not to interfere in the present work. Thallium, lead, bismuth, and polonium* would also be extracted under these conditions, but do not occur as products of low-energy fission. The daughter product of tin by β^-decay is antimony, which is not extracted by dithizone. The method as developed for use in this investigation was rapid extraction of tin from fission, followed by rapid back-extraction of the newly-formed antimony from this solution.

Indication was given in some experiments that exchange between the stannous and stannic ions in the tartrate solution was incomplete, and proceeded with a half-time of the order of five or ten minutes. This half-time value is very uncertain. As complete recovery of tin was of little consequence in most cases, this phase of the chemistry was not investigated further.

Since the activated tin had all to be in its lower valence state, the very strong oxidizing action of the γ-radiation and of the recoiling fission fragments in aqueous media made it impractical to irradiate a solution. This suggested that it would be desirable to irradiate a solid, readily-soluble, anhydrous compound of tetravalent uranium. The compound which was found to suit the conditions best was pyridinium hexachlorouranate(IV)—$(PyH)_2UCl_6$. This compound, mentioned by STARKE[18] and referred to vaguely by others, but not specifically described in the literature, will be discussed in a separate communication. It is stable against oxidation by air, is not deliquescent, and is rapidly soluble in slightly acid media. Its preparation is briefly described later in the present paper.

Procedure

Irradiate $(PyH)_2UCl_6$ (Note 1). Dissolve the target in 10 ml NH_4Ac (10 per cent), to which has been added about 0·5 mg tin (stannous) carrier. To this solution add 10 ml 10 per cent potassium sodium tartrate (KNaT), and adjust to pH 8·5 with 2–4 ml of 4M NH_4OH (Note 2). Extract tin by shaking for 10–15 seconds with 10 ml of 0·01 per cent dithizone in CCl_4. Shake this solution once with 5 per cent NH_4Ac–5 per cent KNaT–pH 8·5 solution (Note 3).

Antimony can be milked from the tin by shaking successively the whole dithizone-CCl_4 phase, or portions thereof, at regular intervals with 10 ml of NH_4Ac-KNaT solution (Note 4). Zero time for the extraction was taken at the end of the shaking period. Since shaking times and solution volumes were equal in all cases, no error is introduced in half-life measurement (this is not the case, however, in fission-yield measurements). The antimony isotopes can now be counted in solution. In a typical experiment, the tin can be isolated about 45 seconds after the end of irradiation. Antimony can be separated from the tin about half a minute later, and thereafter at intervals of two or three minutes.

Notes

(1) The amount of target used is, of course, arbitrary, but the procedure was found to work best for quantities between 25 and 300 mg.

(2) Ammonium acetate is used as buffer, while the tartrate serves to prevent precipitation of uranium and tin from the basic solution, and complexes the antimony so that it does not adsorb on the walls of the separatory funnel. The solution is so buffered that its pH slowly approaches a value of 9·5 at 1M in NH_4OH. Since even at this high pH, stannous tin is well extracted, fine adjustment of the pH at this point is unnecessary.

* It was found during the course of this work that polonium is quantitatively extracted by dithizone solution in carbon tetrachloride at pH 8·5 and pH 3, but not from 1M HCl. The pH-dependence of this extraction makes possible a rapid and clean separation of polonium from lead.

[17] H. FISCHER and G. LEOPOLD: (1940) *Chem. Ztg.*, **64**, 231.

[18] K. STARKE (1950) *Canad. J. Research*, **B28**, 225; (1950) Personal Communication.

(3) The main impurities at this point are palladium, cadmium, and indium. The daughter products of all of these also react with dithizone under the conditions used, and thus are not back-extracted in the presence of excess dithizone.

(4) Since the stannous dithizonate complex has a tendency to dissociate, an excess of dithizone must be present. It is also best not to shake too long. The half-life value obtained for Sb^{122} would be particularly sensitive to tin contamination. The values found in this work, however, were in consistently good agreement with previous values.[12, 13] From this fact, it was computed that tin impurity in the antimony samples cannot have been in excess of about 2 per cent.

About 10 sec of vigorous shaking is recommended. It was observed in similar cases that back-extraction of metals from dithizone-CCl_4 solution is essentially complete within 3–4 sec. On the basis of this fact and of tracer tests showing antimony to be extracted to the extent of less than 0·02 per cent, it has been assumed that the chemical yield of antimony in the back-extraction process is 100 per cent.

Tracer tests were carried out using 19-d Rb^{86}, 60-d Sb^{124}, 77·7-h Te^{132}, and a mixture of all the fission products. The results are given in Table 2.

TABLE 2.—TRACER TESTS OF THE TIN SEPARATION PROCEDURE

Tracer element	Separation factor*	
	CCl_4 phase (tin)	Back extract (antimony)
Rb†	5×10^4	10^5
Sb	5×10^3	10^4
Te	10	>200
Fission mixture	10^3	10^3

* The separation factor is equal to the activity of the original solution divided by the activity of the extract listed. A high value for the factor indicates a good separation.

† Rb tracer was used to determine the amount of contamination introduced by mere mechanical entrainment of the aqueous phase in the carbon tetrachloride phase.

The data for Rb^{86} in Table 2 indicate clearly that it is not necessary to include a washing step, provided that the phases are carefully separated. It is also shown in Table 2 that the separation is good from antimony, and adequate from tellurium—the immediate disintegration products of tin—and good from the fission products in general. In the tin dithizonate solution, the separation is poor from palladium, cadmium, and indium, but the antimony back-extract is essentially free from these low-fission-yield contaminants (see previous discussion).

It is evident that this procedure is not readily applicable to studies of high-energy fission, where the yields of cadmium and indium become very high, and where spallation-produced isotopes of lead, thallium, bismuth, and polonium will become contaminants. It is also not applicable to studies of neutron-deficient tin isotopes, where indium is the daughter product.

Preparation of the Target Compound

The most satisfactory method of preparing the target compound is as follows: Electrolyse a solution of UO_2Cl_2 to prepare tetravalent uranium. To the reduced solution, add an excess of pyridinium hydrochloride, evaporate the water, and heat until most of the excess pyridine hydrochloride has distilled off. Add chloroform to precipitate $(PyH)_2UCl_6 \cdot n$Py, and to dissolve the excess pyridine hydrochloride. Wash the precipitate several times with chloroform, warming slightly each time. Dry, and heat at 50–60°C for about twenty-four hours.

Because stannous tin is such a strong reducing agent, it is necessary to avoid all traces of hexavalent uranium. It is thus advisable to electrolyse until much of the uranium has been reduced to the trivalent form, and to use pure pyridine hydrochloride. The final dried compound is quite stable against air oxidation, and will not absorb air moisture if all the pyridine hydrochloride has been removed. The composition is probably $(PyH)_2UCl_6$—39 per cent uranium.

Counting Techniques

The antimony samples were counted as 10-ml portions of the acetate-tartrate extract, placed in identical plastic cuvettes, in identical positioning, over an inverted externally quenched end-window Geiger-Muller tube. Since all the β-radiations involved are very energetic, it was assumed that they are counted with approximately equal efficiency. In one test, two otherwise identical samples were counted, one in solution, and the other as a thin solid sample. These gave essentially identical decay-curves. Background was measured frequently during the course of the experiments to guard against the effect of fluctuations in the pile level.

RESULTS

Analysis of Decay-curves; Half-lives

The method of curve analysis used was to fit to the experimental points a constructed curve for the decay of the 23·1-min Sb^{131}–25-min Te^{131} pair, subtracting whatever long-lived background (as 4·6-h Sb^{129}–70-min Te^{129}) was necessary to obtain a reasonable fit.* Construction of the curve was based on the genetic relationships shown in Table 1, and on equal counting efficiency for antimony-131 and tellurium-131, as demonstrated earlier by PAPPAS.[12] This constructed curve was then subtracted from the experimental points to give successively the 10-min (Sb^{130}) and 2-min (Sb^{132}) components. A typical analysis is shown in Fig. 1. The decay-curves of these various components were extrapolated to the time of separation of antimony, and the values thus obtained for their original activities were taken as proportional to the activities of the respective tin parents at the beginning of the growth period.†

Since these growth periods were of equal length, the extrapolated activities for the several antimony samples could be compared. Usually four or six such antimony samples were counted for each tin separation, giving four to six points on the tin decay-curve. Such a tin decay-curve is shown in Fig. 2.

The half-lives found in the various experiments are given in the following tables (Tables 3 to 7). The limits of error as given were estimated by the authors, based on non-rigorous evaluation of the reliability of the data. The limits of error as calculated from a statistical treatment of the data are smaller than the limits listed. In the case of antimony-130 and antimony-132, for which previous values had been reported, selected values are given. The values reported here for the half-lives of antimony-130 and antimony-132 are only a few selected from many values. The selection was made on the basis of counting statistics, high number of readings, length of exponential decay, and treatment of data. The unreported values were not in disagreement with the selected ones, but were based on too few points to be reliable in determining the final half-life value. The values obtained for antimony-132 are perhaps less reliable because of the possibility of contamination with ≤ 2 per cent tin.

* In these experiments the 70–60-min Sb was never clearly observed, probably due to low yield.[12]

† $D_2(t) = \dfrac{T_1}{T_2 - T_1}(e^{-\lambda_2 \tau} - e^{-\lambda_1 \tau}) \cdot D_1^0 \cdot e^{-\lambda_1 t}$

where 1 and 2 denote respectively the parent and daughter,

$D_2(t)$ = disintegration rate of the daughter at the end of the growth period,

D_1^0 = disintegration rate of the parent at the end of irradiation,

t = decay time of the parent from the end of irradiation to the beginning of growth period of the daughter,

τ = the length of the growth period,

λ and T are respectively the decay constant and half-life. When τ is constant, this becomes

$$D_2(t) = CD_1^0 e^{-\lambda_1 t}.$$

Each antimony sample has a different value for t and gives a corresponding value for $D_2(t)$. A plot of log D_2 *vs*. t gives thus the decay of the parent tin.

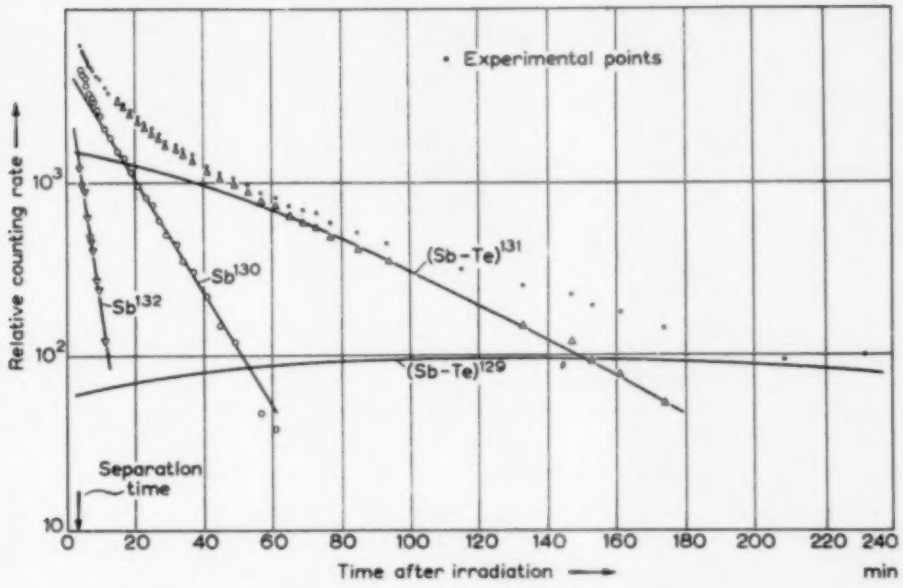

FIG. 1.—A typical analysis of the composite antimony decay-curve.

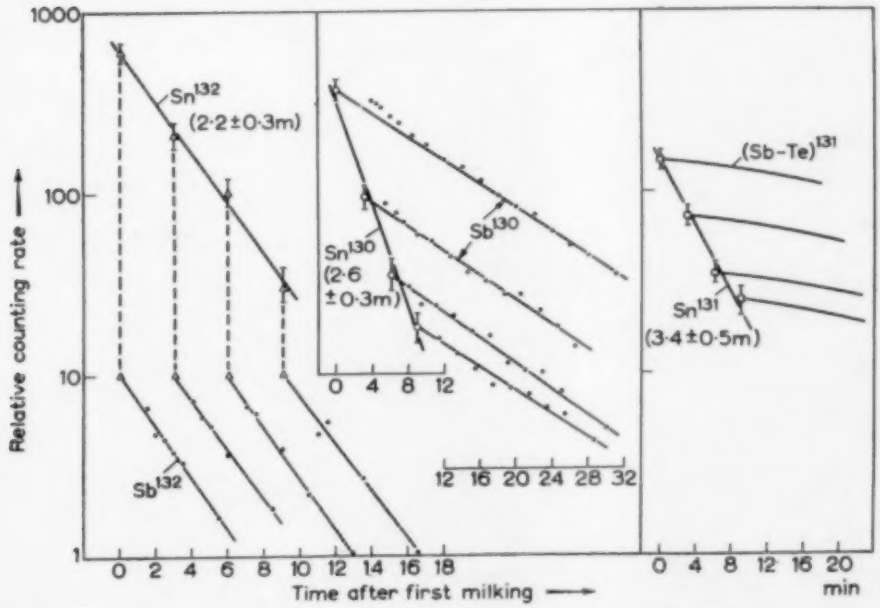

FIG. 2.—Typical decay-curves for the tin activities: Sn^{133}, Sn^{130}, Sn^{131}.

TABLE 3.—HALF-LIFE OF ANTIMONY-130

Sample	Value found, minutes
1	9·6
2	10·0
3	9·0
4	8·6
5	9·1
6	8·8
Average, this work	9·2 ± 0·3
PAPPAS[12]	12 ± 2
BARNES and FREEDMAN[11]	10
FRÄNZ, RODRIGUEZ, and CARMINATTI[19]	10
Selected value	10·0 ± 0·5 min

TABLE 4.—HALF-LIFE OF TIN-130

Experiment	Half-life, minutes
1	2·8
2	3·0
3	2·5
4	2·0
Average	2·6 ± 0·3 min

TABLE 5.—HALF-LIFE OF TIN-131

Experiment	Half-life, minutes	Relative reliability
1	3·0	2
2	2·7	1
3	3·7	3
4	3·7	3
5	3·1	1
Weighted average	3·4 ± 0·5 min	

TABLE 6.—HALF-LIFE OF ANTIMONY-132

Sample	Half-life, minutes
1	2·2
2	2·2
3	2·1
4	2·1
5	1·8
6	2·1
Average, this work	2·1 ± 0·2
PAPPAS[12]	1·9 ± 0·2
COOK[13]	~2
Selected value	2·0 ± 0·2 min

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TABLE 7.—HALF-LIFE OF TIN-132

Experiment	Half-life, minutes
1	2·2
2	2·2
Average	2·2 ± 0·3 min

Fission Yields

The fission yields of the isotopes of antimony have been measured by PAPPAS.[12] Obviously he was not able to make any parent correction in the yields of Sb^{130}, Sb^{131}, and Sb^{132}, because the half-lives of their parents were unknown. Following the discovery of the tin parents of these isotopes, a correction term can be now applied to the yield-values reported in reference (12). This correction is straightforward, and is discussed in detail in reference (3). With the data in reference (12) the following yield values are obtained, with the old ones in parentheses: 10·0-min Sb^{130}, 2·5 ± 0·5 per cent (2·1 per cent); 23·1-min Sb^{131}, $2{\cdot}5_6$ ± 0·2 per cent (1·75 per cent); and 2·0-min Sb^{132}, unchanged ~3 per cent.

An interesting result of the corrected yield-values appears in the mass 131 chain. Using the new value for Sb^{131} and the total yield of (Te^{131m} + Te^{131}) $3{\cdot}0_2$ per cent,[20] one finds the independent yield of (Te^{131m} + Te^{131}) to be 0·46 per cent, giving a fractional chain-yield of 0·15 ± 0·07.

From the postulate of equal charge displacement as modified by PAPPAS,[21] one would expect a fractional yield of 0·12 for these isomers. This thereby gives further support to the reliability of the new postulate of charge division.

It would be interesting to measure the relative fission yields of the new tin isotopes,

[19] I. FRANZ, J. RODRIGUEZ, and H. CARMINATTI (1955) *Z. Naturforsch.*, **10a**, 82.
[20] A. C. PAPPAS, Reference 3, p. 104.
[21] A. C. PAPPAS, Reference 3, pp. 125–132; A. C. PAPPAS, International Conference on the Peaceful Use of Atomic Energy 1955, paper 881.

thereby checking the postulate of PAPPAS[3] and WILES.[1] Owing, however, to uncertainties in chemical exchange and the all too short time available for making absolute β-measurements, no reliable yield measurements have been made.

ACKNOWLEDGEMENTS

The authors wish to express their thanks to the director of the Joint Establishment for Nuclear Energy Research (Kjeller, Norway), Dr. G. RANDERS, for permission to use the reactor for this investigation. The very considerable assistance given by Dr. E. SÆLAND and his group is particularly appreciated. Sincere thanks are extended to Dr. R. A. SHARP for helpful discussions, and to Miss L. GJERTSEN and Mr. J. THOMASSEN for assistance with irradiations and counting of samples.

The authors are indebted to the Royal Norwegian Council for Scientific and Industrial Research, for supporting grants; and to the Nansen Foundation for additional financial aid.

J. Inorganic and Nuclear Chemistry, 1956, Vol. 2, pp. 79–87. Pergamon Press Ltd., London

STRUCTURES OF COMPLEX FLUORIDES—I

POTASSIUM HEXAFLUORO-OSMATE(V), $KOsF_6$

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(*Received* 26 *August* 1955)

Abstract—$KOs^{V}F_6$ is rhombohedral with dimensions $a = 4{\cdot}991 \pm 0{\cdot}001$ Å, $\alpha = 97{\cdot}18 \pm 0{\cdot}02°$, and has atoms in the following positions of space group $R\bar{3}$—C_{3i}^{2}: Os at 0,0,0; K at $\frac{1}{2},\frac{1}{2},\frac{1}{2}$; and six F at $\pm(x,y,z)$; $\pm(z,x,y)$; $\pm(y,z,x)$, where $x = 0{\cdot}717 \pm 0{\cdot}005$, $y = 0{\cdot}789 \pm 0{\cdot}005$, and $z = 0{\cdot}103 \pm 0{\cdot}005$. The structure is a distorted caesium chloride-like arrangement of K and OsF_6 ions in which each complex anion consists of an irregular octahedron of fluorine atoms surrounding a central osium atom. It is similar to, but is of lower symmetry than, the structures reported by other workers for rhombohedral RMX_6 hexafluorides. A prediction for this structure-type that the radius ratio R to X approximates to unity is substantiated. The principal interatomic distances in $KOs^{V}F_6$ are: K–F = 2·84 and 3·17; Os–F = 1·82; F–F = 2·48, 2·66, and 2·87 Å.

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INTRODUCTION

RMX_6 STRUCTURES are classified[1] as (i) undistorted or tetragonally distorted sodium chloride arrangements of R and MX_6 ions; (ii) rhombohedrally distorted caesium chloride arrangements of R and MX_6 groups; and (iii) nickel arsenide-like structures. Among the type (ii) rhombohedral structures, only $BaSiF_6$, $BaGeF_6$[2], and $TlSbF_6$[3] had been described fully when the present investigation started. For these three compounds the proposed space group is $R\bar{3}m$—D_{3d}^{5} and the unimolecular unit cell contains M at 0,0,0; R at $\frac{1}{2},\frac{1}{2},\frac{1}{2}$; and six F at $\pm(x,x,z)$; $\pm(x,z,x)$; $\pm(z,x,x)$. In $BaSiF_6$ and $BaGeF_6$ the parameters x and z (see Table 1) were chosen to give a regular octahedron of fluorine atoms around each atom M and also gave reasonable agreement between observed and calculated X-ray intensities. Since the rhombohedral angles are near 90° (see Table 2), the structure-type was described as a distorted caesium chloride arrangement of R and MX_6 groups. Each atom R is surrounded by twelve X atoms

TABLE 1.—PARAMETERS FOR FLUORINE ATOMS OF RHOMBOHEDRAL RMX_6 STRUCTURES BASED ON SPACE GROUP $R\bar{3}$

	Fluorine Parameters			Space Group Reported	Author
	x	y	z		
$BaSiF_6$	0·746	= 0·746	0·085	$R\bar{3}m$	HOARD and VINCENT[4]
$BaGeF_6$	0·741	= 0·741	0·086	$R\bar{3}m$	HOARD and VINCENT[4]
$TlSbF_6$	0·73	= 0·73	0·10	$R\bar{3}m$	SCHREWELIUS[3]
$BaRuF_6$	—	—	—	$R\bar{3}m$	WEISE and KLEMM[6]
$KRuF_6$	0·728	= 0·728	0·085	$R\bar{3}m$	WEISE and KLEMM[6]
$RbRuF_6$	0·736	= 0·736	0·086	$R\bar{3}m$	WEISE and KLEMM[6]
$CsRuF_6$	0·748	= 0·748	0·089	$R\bar{3}m$	WEISE and KLEMM[6]
$KOsF_6$	0·717	0·789	0·103	$R\bar{3}$	Present work

[1] WYCKOFF, R. W. G. (1951), *Crystal Structures*, vol. II. New York: Interscience Publishers.
[2] HEPWORTH, M. A., ROBINSON, P. L., and WESTLAND, G. J., (1954). *J. Chem. Soc.* p. 4268.
[3] SCHREWELIUS, N. (1942). *Ark. Kemi. Mineral. Geol.* **B16**, 1.

from eight different MX_6 octahedra to give an RX_{12} co-ordination group. HOARD and VINCENT[4] predicted that such a structure would be stable only if the radius ratio of R to X did not differ appreciably from unity. They also suggested that the anion octahedra might not be exactly regular, but might be slightly stretched along their three-fold axes.

The present investigation aimed at detailed structure determinations of a series of new complex hexafluorides of ruthenium, osmium, and iridium, prepared recently in this laboratory[2, 5] and some of which are listed in Table 2. Their unit-cell dimensions

TABLE 2.—UNIT-CELL DIMENSIONS OF RHOMBOHEDRAL RMX_6 STRUCTURES

	a (Å)	α (°)	Author
$BaSiF_6$	4·75	97·97	HOARD and VINCENT[4]
$BaGeF_6$	4·83	98·02	HOARD and VINCENT[4]
NH_4SbF_6	5·10	96·50	SCHREWELIUS[3]
$RbSbF_6$	5·11	96·50	SCHREWELIUS[3]
$CsSbF_6$	5·32	96·90	SCHREWELIUS[3]
$TlSbF_6$	5·15	96·00	SCHREWELIUS[3]
$KRuF_6$	4·96	97·5	WEISE and KLEMM[6]
	4·97	97·4	Present work
$RbRuF_6$	5·08	97·0	WEISE and KLEMM[6]
	5·07	96·9	Present work
$CsRuF_6$	5·25	96·2	WEISE and KLEMM[6]
	5·25	96·3	Present work
$BaRuF_6$	4·87	98·0	WEISE and KLEMM[6]
	4·89	97·9	Present work
$KOsF_6$	4·991	97·18	Present work
$CsOsF_6$	5·28	96·1	Present work
$KIrF_6$	4·98	97·4	Present work
$CsIrF_6$	5·27	96·2	Present work
$BaIrF_6$	4·90	97·8	Present work

indicated that they were probably of the $BaSiF_6$ type, but accurate X-ray intensity data subsequently showed that, in some cases at least, structures were incompatible with space group $R\bar{3}m$—D_{3d}^5.

Since the completion of the work described below, WEISE and KLEMM[6] have assigned the structures of $BaRuF_6$, $KRuF_6$, $RbRuF_6$, and $CsRuF_6$ also to space group $R\bar{3}m$. Although there is broad agreement between their observed and calculated X-ray data, certain anomalies appear to exist, and it seems not yet certain that the structures proposed by WEISE and KLEMM are accurate in detail. Complex fluorides, including those of vanadium, tantalum, and niobium, are also the subject of current investigation at Cambridge by COX.[7] Thus, since it offers a basis of comparison for other transition-element complex fluorides which are now under examination in this laboratory and elsewhere, the present paper describes the results of a detailed structural analysis of $KOsF_6$.

[4] HOARD, J. L., and VINCENT, W. B. (1940). *J. Amer. Chem. Soc.* **62**, 3126.
[5] HEPWORTH, M. A., PEACOCK, R. D., and ROBINSON, P. L. (1954). *J. Chem. Soc.* p. 1197.
[6] WEISE, E., and KLEMM, W. (1955). *Z. anorg. Chem.* **279**, 74.
[7] COX, B. (1955). Private communication.

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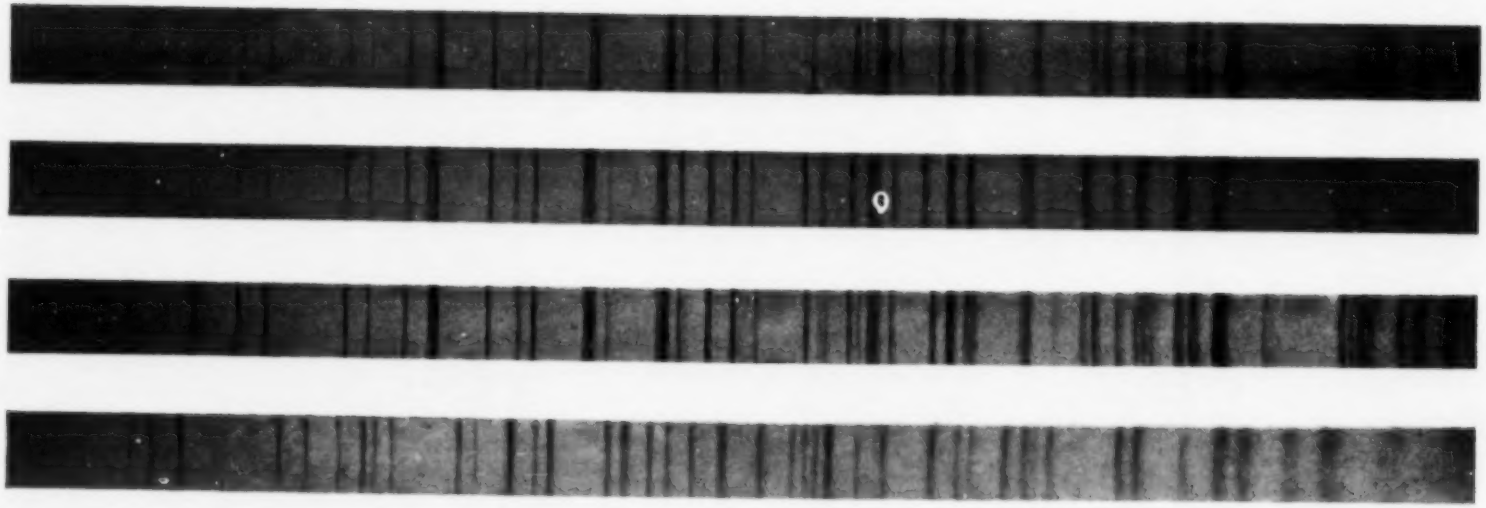

Fig. 1.—X-Ray powder photographs of $KRuF_6$, $KOsF_6$, $FIrF_6$ and $NaOsF_6$:
(i) $KRuF_6$
(ii) $KOsF_6$
(iii) $KIrF_6$
(iv) $NaOsF_6$

EXPERIMENTAL

X-ray powder photographs of $KOsF_6$ prepared by HEPWORTH, ROBINSON, and WESTLAND.[2] (Found: Os 54·6, F 33·4 per cent; equivalent, 347. $KOsF_6$ requires Os 55·5, F 33·1 per cent; equivalent, 343) were taken at 18 ± 2°C in a 19-cm cylindrical camera using crystal-reflected Fe Kα radiation (α_1, 1·93597; α_2, 1·93991 Å) from a lithium fluoride monochromator. Since the material decomposes in moist air, thin-walled glass X-ray-specimen capillaries, 0·5 mm diameter (supplied by Pantak Ltd., Slough), were filled and sealed off in a dry-box. Duplicate films, which showed low background intensities, were microphotometered with a Dobson-type instrument built from a design by TAYLOR,[8] and values of the integrated intensities in arbitrary units were obtained by measuring areas under the plotted photometer curves with a planimeter.

For any line in a powder photograph, the intensity is given by

$$I = \text{constant} \,.\, F^2_{hkl} \,.\, \frac{1 + \cos^2 2\alpha \,.\, \cos^2 2\theta}{\sin^2 \theta \,.\, \cos \theta} \,.\, p \,.\, A \,.\, \exp\left[-B(\sin\theta/\lambda)^2\right],$$

where α is the angle of reflexion in the monochromator, and other symbols have their usual meanings. In calculating intensities, HÖNL's absorption-edge effect was taken into account (see JAMES,[9] 1948, vol. 2, pp. 160, 608) and the absorption and arbitrary temperature factors were obtained by standard methods. For the determination of unit-cell dimensions, the extrapolation function used by NELSON and RILEY[10] was employed.

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RESULTS

All observed X-ray reflexions from $KOsF_6$ were indexed on a unimolecular rhombohedral cell of dimensions $a = 4{\cdot}991 \pm 0{\cdot}001$ Å, $\alpha = 97{\cdot}18 \pm 0{\cdot}02°$. The corresponding trimolecular hexagonal cell has dimensions $a = 7{\cdot}487 \pm 0{\cdot}001$, $c = 7{\cdot}487 \pm 0{\cdot}001$ Å, $c/a = 1{\cdot}0000 \pm 0{\cdot}0002$. The occurrence of sharply resolved reflexions at Bragg angles up to 80° enabled these dimensions to be calculated to within the limits indicated. Values of $\sin^2\theta$ calculated from the dimensions and corrected for systematic errors (TAYLOR and FLOYD[11]) are compared with observed $\sin^2\theta$ values in Table 3.

X-ray powder photographs of $KRuF_6$, $KOsF_6$, $KIrF_6$, and $NaOsF_6$ are reproduced in Fig. 1. It seems probable from the close similarities of the first three photographs that $KRuF_6$ and $KIrF_6$ are isostructural with $KOsF_6$. Small differences in the positions of corresponding reflexions are due, of course, to the different unit-cell sizes. In addition, there are intensity differences which may not be due solely to the different atomic scattering factors of Ru, Os, and Ir, but which may be a result of slight differences in the atomic positions. By comparing Figs. 1(iv) and 1(ii), it is apparent that the structure of sodium hexafluoro-osmate is quite different from that of potassium hexafluoro-osmate. Preliminary trials showed that the $KOsF_6$ structure was similar to that proposed by HOARD and VINCENT[4] for $BaSiF_6$. Following these authors, we allocated $KOsF_6$ to space-group $R\bar{3}m$ (No. 166; International Tables,[12] 1952, vol. 1, p. 272) with Os, K, and F atoms in positions (*a*), (*b*), and (*h*) respectively. However, despite systematic variation of the fluorine-atom parameters *x* and *z*, the agreement between observed and calculated intensities was always unsatisfactory.

If Os is placed at the cell origin it is unlikely from chemical and structural considerations that K is other than at $\frac{1}{2},\frac{1}{2},\frac{1}{2}$. Moreover, movement of K along the trigonal axis from $\frac{1}{2},\frac{1}{2},\frac{1}{2}$ did not improve the intensity agreement. Thus, assuming Os and K to be at 0,0,0 and $\frac{1}{2},\frac{1}{2},\frac{1}{2}$ respectively, the only other possible space-groups are R32 (No. 155) and $R\bar{3}$ (No. 148). These were considered in turn, and, after exhaustive trial and error, excellent intensity agreement was obtained by assigning the structure to the latter space-group $R\bar{3}$—C^2_{3i} with atoms in the following positions: Os in (*a*) at 0,0,0; K in (*b*) at $\frac{1}{2},\frac{1}{2},\frac{1}{2}$; and six F in (*f*) at $\pm(x,y,z)$; $\pm(z,x,y)$; $\pm(y,z,x)$, with $x = 0{\cdot}717 \pm 0{\cdot}005$, $y = 0{\cdot}789 \pm 0{\cdot}005$, and $z = 0{\cdot}103 \pm 0{\cdot}005$. As shown in Table 3, there are no systematic absences; all observed reflexions are quantitatively accounted for by the proposed structure, and no possible reflexion remains unobserved. It should be noted that, although powder reflexions with indices *pqr* and *prq* are coincident, the structure amplitudes F_{pqr} and F_{prq} are in general unequal.[13] For space group $R\bar{3}m$ (e.g., $BaSiF_6$), $F_{pqr} = F_{prq}$. The mean discrepancy in structure-amplitude agreement ($R = \Sigma(|\,Fo\,| - |\,Fc\,|)/\Sigma|\,Fo\,|$) for the proposed structure is less than 0·03 (thirty-eight reflexions).

[8] TAYLOR, A. (1951). *J. Sci. Instrum.* **28**, 200.
[9] JAMES, R. W. (1948). *The Crystalline State*. London: Bell and Sons.
[10] NELSON, J. B., and RILEY, D. P. (1945). *Proc. Phys. Soc.* **57**, 160.
[11] TAYLOR, A., and FLOYD, R. W. (1950). *Acta Cryst.* **3**, 285.
[12] *International Tables for X-ray Crystallography* (1952). Birmingham: Kynoch Press.
[13] HENRY, N. F. M., LIPSON, H., and WOOSTER, W. A. (1951) *The Interpretation of X-ray Diffraction Photographs*. London: Macmillan & Co.

Table 3.—Calculated and observed X-ray data for potassium hexafluoro-osmate(V), $KOsF_6$ (Fe $K\alpha$ radiation)

hkl	$\sin^2\theta$		Relative Intensities		
	Calc.†	Obs.	Calc.		Obs.
100	0·0393	0·0394	905		920
10$\bar{1}$	0·0676	0·0673	1141		1228
110	0·0897	0·0897	1150		1144
11$\bar{1}$	0·1065	0·1064	532		526
111	0·1511	0·1510	20		vvw
200	0·1568	0·1568	435		435
20$\bar{1}$ 02$\bar{1}$	0·1734	0·1733	208 37	245	233
2$\bar{1}\bar{1}$	0·2015	0·2015	434		418
210 120	0·2182	0·2181	347 232	579	581
21$\bar{1}$ 12$\bar{1}$	0·2238	0·2238	1131 640	1771	1733
202	0·2684	0·2683	563		538
211	0·2907	0·2905	320		363
212 122	0·3074	0·3076	276 325	601	590
22$\bar{1}$ 300	0·3521	0·3521	485 165	650	639
30$\bar{1}$ 03$\bar{1}$	0·3577	0·3576	375 276	1172	1105
220	0·3577		521		
3$\bar{1}\bar{1}$	0·3744	0·3742	143		154
31$\bar{1}$ 13$\bar{1}$	0·4190	0·4188	224 131	355	392
310 130	0·4247	0·4249	502 593	1568	1595
222	0·4247		473		
302 032	0·4414	0·4413	308 195	606	642
221	0·4414		103		
3$\bar{1}$2 $\bar{1}$32	0·4693	0·4693	594 277	871	851
312 132	0·4915	0·4915	357 341	698	636
311	0·5083	0·5080	284		240
32$\bar{1}$ 23$\bar{1}$	0·5584	0·5585	422 284	706	690
320 230	0·5752	0·5751	98 179	374	386
223	0·5752		97		
303 222	0·6031 0·6031	0·6035*	487 130	617	605
322 232 40$\bar{1}$ 04$\bar{1}$	0·6197	0·6191	159 76 77 240	552	500

TABLE 3.—*continued*

hkl	$\sin^2\theta$ Calc.†	$\sin^2\theta$ Obs.	Relative Intensities Calc.	Relative Intensities Obs.
4$\bar{1}$1	0·6253	0·6259	446	850
400	0·6253		365 811	
313	0·6420	0·6419	76	311
133			265 341	
321	0·6700	0·6703	282	691
231			390 672	
402	0·6922	0·6922	324	1350
042			484	
41$\bar{1}$	0·6922		211	
14$\bar{1}$			305 1324	
4$\bar{1}$2	0·7090	0·7088	195	900
$\bar{1}$42			205	
410	0·7090		160	
140			278 838	
412	0·7535	0·7527	92	184
142			104 196	
323	0·7591	0·7590	185	564
233			350 535	
33$\bar{1}$	0·7759	0·7747	145	106
422	0·8038	0·8037	303	992
411	0·8038		555	
330			202 1060	
332	0·8259	0·8258	507	1583
403	0·8427	0·8426	255	
043			158	
42$\bar{1}$	0·8427		173	
24$\bar{1}$			114	
322	0·8427		289 1496	
4$\bar{1}$3	0·8706	0·8704	492	1818
$\bar{1}$43			344	
420	0·8706		351	
240			553 1740	
413	0·8928	0·8927	510	1829
143			403	
422	0·8928		576	
242			240 1729	
331	0·9095	0·9092	135	160
5$\bar{1}$1	0·9541	0·9541	478	mw
333			333 811	
50$\bar{1}$	0·9596	0·9596	591	m
05$\bar{1}$			940 1531	
421	0·9764	0·9762	332	m
241			433	
500	0·9764		310	
32$\bar{3}$			240	
23$\bar{3}$	0·9764		358 1673	

* Reflexions at higher Bragg angles than this were resolved into α_1- and α_2-components, so that "observed" $\sin^2\theta$ values are listed as weighted mean values of the doublets.

† Values calculated from the cell dimensions and corrected for systematic errors.

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DISCUSSION

The $KOsF_6$ structure is most simply described as a caesium chloride arrangement of K atoms and OsF_6 groups with a rhombohedral angle near 97° instead of 90°. Each OsF_6 complex consists of six fluorine atoms each at a distance of 1·82 Å from the central osmium atom, and forming around it an irregular octahedron (see Fig. 2). Contrary to the possibility mentioned by HOARD and VINCENT,[4] the fluorine-atom octahedra are not stretched but are compressed along their three-fold axes. As a consequence, each fluorine has four fluorine-atom neighbours in its own OsF_6 group, two at distances of 2·66 Å and two at 2·48 Å. Although the former distance is in reasonable agreement with the fluorine ionic radius (1·33–1·36 Å) or with the fluorine

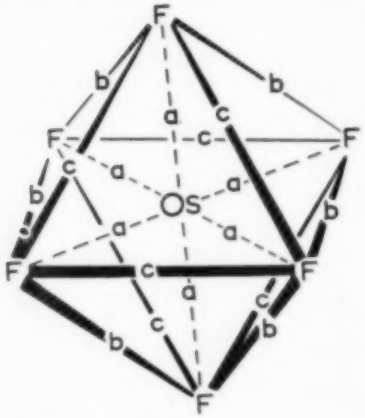

FIG. 2.—The octahedral complex OsF_6; $a = 1{\cdot}82$; $b = 2{\cdot}48$; $c = 2{\cdot}66$ Å.

van der Waals radius (*ca.* 1·35 Å), the latter F–F distance is surprisingly short. It is clear that the bonding within the OsF_6 complex is not ionic. The magnetic moment observed for $KOsF_6$ (3·2 B.M.; see HEPWORTH, ROBINSON, and WESTLAND[2]) corresponds with that calculated (3·88 B.M.) for octahedral $6sp^35d^2$ hybridized covalent bonding of the Os(V). The octahedral covalent-radii for Os(II), Os(IV), and Os(VI) are given by PAULING[14] as 1·33, 1·37, and 1·29 Å respectively, so that the Os(V) radius is probably not less than 1·3 Å. If the fluorine covalent-radius is 0·6 Å, then the calculated Os–F distance (*ca.* 1·9 Å) is larger than the distance observed in $KOsF_6$ (1·82 Å). If the bonding is assumed to be ionic with $r_{Os^{5+}} \approx 0{\cdot}6$ Å, the expected Os–F distance (*ca.* 1·9 Å) is again greater than that observed.

The OsF_6 octahedra are oriented in such a way that six fluorine atoms from six different groups surround each potassium atom to form a puckered ring with a K-F distance of 2·84 Å. In addition, the potassium is co-ordinated by six more fluorine atoms, each at 3·17 Å,—three from an OsF_6 octahedral unit above it and three from a corresponding unit below it. Thus, each alkali-metal atom is co-ordinated by a total of twelve fluorine atoms to give a KF_{12} complex with an average K–F distance of 3·0 Å If the standard univalent radii of K^+ and F^- are taken as 1·33 and 1·36 Å respectively then the calculated K–F distance (corrected for a co-ordination number of 12 and assuming the Born exponent $n = 8$; see PAULING[14]) is 2·97 Å.

[14] PAULING, L. (1940). *The Nature of the Chemical Bond*, 2nd ed., Oxford: The University Press.

As an alternative description, the $KOsF_6$ structure consists of equispaced planes of atoms perpendicular to the [111] direction, the unit-cell repeat distance consisting of six planes. These are shown in Fig. 3 at heights 0, 1, 2, 3, 4, 5, and 6 = 0 along the

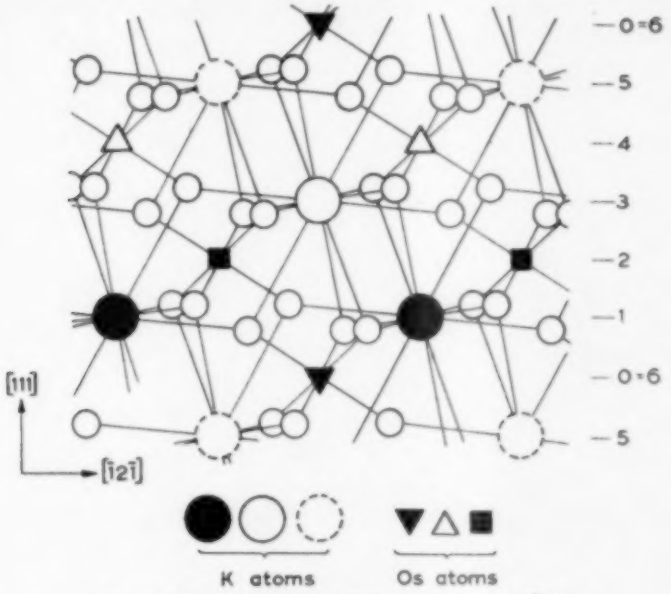

FIG. 3.—Projection of the $KOsF_6$ structure along [1̄01].

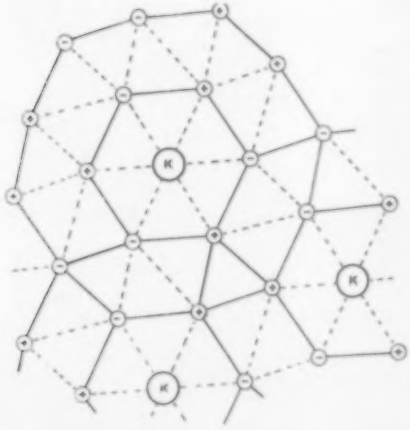

FIG. 4.—Puckered sheet of K and F atoms; + and − signs represent F atoms 0·27 Å above and 0·27 Å below the plane of the K atoms respectively.

trigonal axis. Planes 1, 3, and 5 consist of sheets of fluorine and potassium atoms. Since the fluorine atoms are 0·27 Å above, or the same distance below, each plane of the potassium atoms, these sheets are slightly puckered. One such sheet is reproduced as Fig. 4, in which the small displacements above and below the plane are shown as + and −. The figure shows that each potassium has six neighbouring fluorine atoms

approximately in its own plane and then twelve next-nearest fluorine ligands in the same sheet. As might be expected from their similarity in sizes, the K and F atoms are nearly close-packed in two dimensions. In the puckered ring of fluorine atoms surrounding each potassium, the F–F distance is 2·87 Å, and is not much different from the shortest K–F distance (2·84 Å).

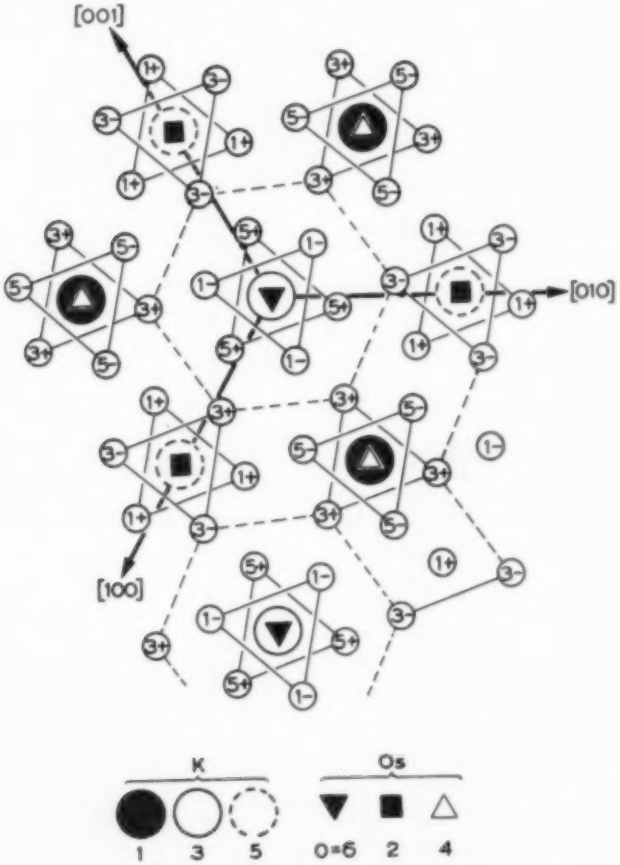

Fig. 5.—Projection of the $KOsF_6$ structure along [111].
● 1 ○ 3 ○ 5 } K atoms in odd planes
▼ 0 = 6 ■ 2 △ 4 } Os atoms in even planes
$n+$ and $n-$ F atom 0·27 Å above or below plane "n"
"n" = 1, 3, 5.

The osmium atoms are at heights 0, 2, 4, and 6 = 0 (see Fig. 3) sandwiched between the sheets of fluorine and potassium atoms.

According to the electrostatic valence rule,[13] each F^- receives $5/6^+$ units of charge from its neighbouring Os^{5+} ion, leaving $1/6^-$ units of charge to be balanced by neighbouring K^+ ions. Since each K^+ has twelve fluorine ligands, then each fluorine must have *two* neighbouring potassium ions; these are at distances of 2·84 and 3·17 Å. Fig. 3 shows that each fluorine atom is bonded to three metal atoms—one Os and two K.

TABLE 4.—INTERATOMIC DISTANCES FOR $KOsF_6$

(i) Observed structure, (ii) and (iii) hypothetical structures; see text
(co-ordination numbers are given in parentheses)

	Fluorine Parameters			Interatomic Distances, Å			
	x	y	z	Os–F	K–F	F–F	Os–K
(i)	0·717	0·789	0·103	(6) 1·82	(6) 2·84 (6) 3·17 } 3·01	(2) 2·48 (2) 2·66 (2) 2·87 } 2·67	(2) 3·74 (6) 4·50
(ii)	0·753 = 0·753		0·103	(6) 1·80	(6) 2·82 (6) 3·15 } 2·99	(2) 2·47 (2) 2·62 (2) 2·86 } 2·65	(2) 3·74 (6) 4·50
(iii)	0·728 = 0·728		0·095	(6) 2·01	(6) 2·74 (6) 3·07 } 2·91	(2) 2·75 (2) 2·75 (2) 2·75 } 2·75	(2) 3·74 (6) 4·50

A projection of the $KOsF_6$ structure along its trigonal axis is shown in Fig. 5, and a summary of the principal interatomic distances is given in Table 4.

It is important to consider the exact nature of the difference between the structure for $KOsF_6$ proposed in the present paper and that proposed by WEISE and KLEMM[6] for $KRuF_6$. If the fluorine-atom parameters x and y for $KOsF_6$ each equalled 0·753 (the mean of the observed values 0·717 and 0·789), then $KOsF_6$ and the $KRuF_6$ would be isostructural (see Table 1). However, the parameters $x = y = 0{\cdot}753$ and $z = 0{\cdot}103$ would give the interatomic distances listed in Table 4. Parameters $x = y = 0{\cdot}728$ and $z = 0{\cdot}095$ would give a perfectly regular OsF_6 octahedron and six equal F–F distances (also see Table 4). The significant common feature of the two hypothetical structures is that they give K–F distances shorter than those found in the observed structure. The structure type, as in so many other examples, is determined primarily by the packing of the large atoms, in this case potassium and fluorine.

The prediction by HOARD and VINCENT[4] that the structure is stable only if the radius ratio of R to X is not much less than unity follows from the approximate close-packing of the fluorine atoms around the potassium. It is therefore not unexpected that $NaOsF_6$ ($r_{Na^+} = 0{\cdot}95$ Å) and $KOsF_6$ ($r_{K^+} = 1{\cdot}33$ Å) are not isostructural. The X-ray photographs of the salts are quite different (see Fig. 1); that of $NaOsF_6$ has been indexed on the basis of a monoclinic cell of dimensions $a = 4{\cdot}88$, $b = 2{\cdot}68$, $c = 4{\cdot}41$ Å, $\beta = 93{\cdot}4°$, and a detailed analysis is proceeding. $AgOsF_6$ ($r_{Ag^+} = 1{\cdot}26$ Å), gives an X-ray photograph similar to that of $NaOsF_6$.

Acknowledgements—We thank Dr. P. L. ROBINSON for his interest and encouragement, and we acknowledge a grant to one of us (K. H. J.) from the Royal Society for construction of X-ray equipment. The work was carried out during the tenure of a British Titan Products Fellowship (M. A. H.) and a Charles Norton Levin Studentship (G. J. W.).

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J. Inorganic and Nuclear Chemistry, 1956, Vol. 2, pp. 88–94. Pergamon Press Ltd., London

PSEUDO-HALOGEN DERIVATIVES OF MONOSILANE

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(*Received* 26 *July* 1955)

Abstract—Silyl *iso*-cyanide, SiH_3NC, and silyl *iso*-thiocyanate, SiH_3NCS, have been prepared and characterized by the measurement of some of their physical properties. Some of the chemical properties of these compounds have also been studied. Unsuccessful attempts to prepare silyl *iso*-cyanate, SiH_3NCO, have been made. Several of the fundamental infra-red absorption bands of silyl *iso*-cyanide and *iso*-thiocyanate have been measured.

In this paper the preparation, properties, and reactions of silyl *iso*-cyanide, SiH_3NC, and silyl *iso*-thiocyanate, SiH_3NCS, are described. These compounds are formally inorganic analogues of methyl *iso*-cyanide and methyl *iso*-thiocyanate, and as such they might have been expected to exhibit somewhat similar properties. However, it has been shown in recent papers[1a–c] that both the physical and chemical properties of most silyl compounds are greatly different from those of their methyl analogues, chiefly because of the ability of silicon to increase its co-ordination number to above 4, and to accept π-bonds from elements of Groups V, VI, and VII. It was the purpose of this research, therefore, to investigate the extent of the difference between analogous silyl and methyl pseudo-halides.

Silyl *iso*-cyanide, SiH_3NC, has been prepared previously[2] from silyl iodide and silver cyanide, but it was reported as silyl cyanide, SiH_3CN. No complete analysis was carried out on the compound and no chemical properties were given. The only physical property reported was a melting-point. No silyl thiocyanate derivatives have so far been described.

Silyl *iso*-cyanide was prepared in yields of over 90 per cent by the action of silyl iodide vapour on silver cyanide at room temperature, viz:

$$SiH_3I + AgNC \rightarrow SiH_3NC + AgI$$

It was also prepared from silyl iodide vapour and mercuric cyanide at slightly elevated temperatures.

The melting-point of silyl *iso*-cyanide was 32·4° (32·3° from the point of intersection of vapour pressure curves of solid and liquid). The higher melting-point, 34°, previously reported for the compound[2] was presumably caused by a too rapid rate of heating. The solid has an extremely high vapour pressure near its melting-point, and an insulating cushion of vapour is readily formed between the solid and the sides of the melting-point tube. The liquid supercooled greatly, and the freezing-point (three determinations) was 24·0–24·1°. For the solid, the vapour pressures in

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[1] (a) Emeléus, MacDiarmid, and Maddock, *J. Inorg. Nucl. Chem.*, **1**, 195, (1955).
[1] (b) Aylett, Emeléus, and Maddock, *J. Inorg. Nucl. Chem.*, **1**, 187, (1955).
[1] (c) Stone and Seyferth, *J. Inorg. Nucl. Chem.*, **1**, 112, (1955).
[2] Emeléus, Maddock, and Reid, *J. Chem. Soc.*, 353, (1941).

the range −20° to 31° were represented by the equation $\log_{10} P = -\frac{2550}{T} + 10{\cdot}951$; the molar heat of sublimation in this range was 11,670 cal/mol, and the calculated vapour pressure at 0·0° was 4·14 cm. For the liquid, the vapour pressures in the range 26° to 46° were represented by the equation $\log_{10} P = -\frac{1567}{T} + 7{\cdot}735$; the molar heat of vaporization in this range was 7169 cal/mol; TROUTON's Constant was 22·2, and the boiling-point (extrapolated) 49·6 ± 0·3°. Silyl *iso*-cyanide was found to be a colourless solid which readily sublimed *in vacuo* at room temperatures to form long crystals up to 2 cm in length. It was not spontaneously inflammable in air, but burned with a bright yellow flame when ignited. It decomposed very slowly in the dark at room temperatures over a period of one to two years to an extent of about 90 per cent, as indicated by the equation below,

$$2\,x\mathrm{SiH_3NC} \rightarrow x\mathrm{SiH_4} + x\mathrm{HCN} + [\mathrm{SiHCN}]_x.$$

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Decomposition was greatly accelerated by traces of mercury. Silyl *iso*-cyanide also decomposed slightly when held near its boiling-point for several hours. It was hydrolysed rapidly and quantitatively by cold water to form disilyl ether according to the equation below,

$$2\mathrm{SiH_3NC} + \mathrm{H_2O} \rightarrow (\mathrm{SiH_3})_2\mathrm{O} + 2\mathrm{HCN}.$$

It did not react at room temperature in the vapour phase with silver chloride to any appreciable extent.

Silyl *iso*-thiocyanate was prepared in 66 per cent yield by the action of silyl iodide vapour on silver thiocyanate at room temperature, viz:—

$$\mathrm{SiH_3I} + \mathrm{AgNCS} \rightarrow \mathrm{SiH_3NCS} + \mathrm{AgI}.$$

The melting-point of silyl *iso*-thiocyanate was −51·8 ± 0·2°. Vapour pressures in the range −33° to 10° were represented by the equation $\log_{10} P = -\frac{1950}{T} + 8{\cdot}340$; the molar heat of vaporization in this range was 8923 cal/mol; TROUTON's Constant was 25·0; the boiling-point (extrapolated) was 84·0 ± 4°, and the calculated vapour pressure at 0·0° was 1·60 cm. The density at 20·0° was 1·05. Silyl *iso*-thiocyanate was found to be a colourless liquid with a pungent sulphurous acetic-acid-like smell. It slowly decomposed to an extent of 74 per cent during twelve days at room temperature. Hydrogen, monosilane, and an unidentified solid were formed. The *iso*-thiocyanate was not spontaneously inflammable in air, but burned with a blue flame when ignited. It was hydrolysed rapidly by cold water to form disilyl ether. The yield of ether was 46·5 per cent of that calculated from the equation below,

$$2\mathrm{SiH_3NCS} + \mathrm{H_2O} \rightarrow (\mathrm{SiH_3})_2\mathrm{O} + 2\mathrm{HCNS}.$$

An attempt was made to prepare a silyl cyanate by the action of silyl iodide vapour on silver cyanate at room temperature. The desired compound was not obtained, and the reaction proceeded according to the equation below,

$$\mathrm{SiH_3I} + 5\mathrm{AgCNO} \rightarrow \mathrm{Si(NCO)_4} + \mathrm{HOCN} + \mathrm{H_2} + 4\mathrm{Ag} + \mathrm{AgI}.$$

Silyl iodide did not react with potassium cyanate, even after twelve days at room temperature. The action of silyl *iso*-thiocyanate vapour on silver cyanate at room temperature was vigorous, but only $Si(NCO)_4$ and HOCN could be isolated from the reaction products.

It appears highly probable that a replacement or "conversion series" similar to that proposed by Eaborn[3] and extended by Anderson[4] for the preparation of alkyl-substituted silyl derivatives may also exist for unsubstituted silyl compounds. In a previous paper[1a] it was shown that silyl iodide reacted with the appropriate silver salt to form disilyl sulphide or selenide. This fact, together with the methods of preparation of silyl *iso*-cyanide and *iso*-thiocyanate given above, strongly supports such a suggestion.

There is at present insufficient evidence to indicate definitely whether the compounds described in this paper are the normal- or *iso*-derivatives. Hydrolysis cannot be used to distinguish the isomers as with the methyl compounds. The general hydrolysis types are given below,

$$\text{(i)}\ MH_3CH \xrightarrow{H_2O} MH_3CONH_2 \xrightarrow{H_2O} MH_3COONH_4$$

$$\text{(ii)}\ MH_3NC \xrightarrow{H_2O} MH_3NH_2 + HCOOH$$

$$\text{(iii)}\ MH_3CN \xrightarrow{H_2O} MH_3OH + HCN$$

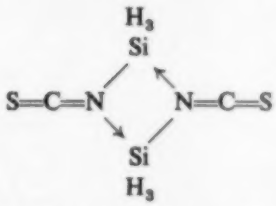
$$\text{(iv)}\ MH_3NC \xrightarrow{H_2O} MH_3OH + HCN$$

followed by $2\ MH_3OH \rightarrow (MH_3)_2O + H_2O$. Both types of hydrolysis can be assumed to take place regardless of whether M is Si or C, but in the case of the methyl compounds reactions (iii) and (iv) are so extremely slow that even the slow reactions (i) and (ii) can take place. However, in the case of silyl compounds, reactions (iii) and (iv) occur almost instantaneously, and consequently there is no time available for the hydrolysis of the CN group while it is still attached to the Si as indicated in equations (i) and (ii). Until there is evidence to the contrary, it seems reasonable to assume that the cyanide is the *iso*-derivative by analogy with the methyl analogue which is formed by the action of methyl iodide on silver cyanide.[5] Both methyl *n*- and *iso*-thiocyanates are asymmetric top molecules,[6] whereas the silyl thiocyanate compound is shown by its infra-red absorption spectrum[7] to be a symmetric top molecule. This implies a linear Si—N—C—S or Si—S—C—N chain, which is more likely for the $Si \leftarrow N{=}C{=}S$ structure produced by π-bonding of the N to the silicon. Consequently the compound is probably silyl *iso*-thiocyanate.

The fact that silyl *iso*-thiocyanate is a symmetric top molecule indicates that there must be strong π-bonding between the nitrogen and silicon. This hypothesis is also supported by the fact that liquid silyl *iso*-thiocyanate is considerably associated

[3] Eaborn, *J. Chem. Soc.*, 3077 (1950).
[4] (a) Anderson and Fischer, *J. Org. Chem.*, **19**, 1296, (1954).
(b) Anderson and Vasta, *ibid.*, 1300.
[5] (a) Gauthier, *Ann. Chim. Phys.*, (iv), 222, (1869).
(b) Gauthier, *Annalen*, 152, 222, (1869).
[6] Beard and Dailey, *J. Amer. Chem. Soc.*, **71**, 929, (1949).
[7] MacDiarmid and Maddock, *J. Inorg. Nucl. Chem.*, (in press).

(TROUTON's Constant, 25·0). This could be explained by a type of *inter*-molecular bonding as shown below



Infra-red absorption spectra of silyl *iso*-cyanide and *iso*-thiocyanate were prepared. Several of the fundamental absorption bands of both compounds were identified. The spectrum of the *iso*-thiocyanate is discussed in greater detail elsewhere.[7]

EXPERIMENTAL

All experimental work was conducted in an all-glass vacuum system, taps being lubricated with Apiezon grease. When an attack on the tap grease was considered likely, the taps were replaced by glass diaphragms, which could be broken electromagnetically as required. Vapour pressure measurements above room temperature were carried out in an all-glass tensimeter.

Silyl iodide was prepared from silane and hydrogen iodide.[11b]

Before any physical or chemical property of the compound under investigation was studied, the purity of the compound was first checked by measuring its vapour pressure at 0·0°.

PRODUCTION AND REACTIONS OF SILYL *ISO*-CYANIDE

Reaction of Silyl Iodide with Silver Cyanide

The reaction was studied by streaming the vapour of silyl iodide (1·020 g) through a horizontal tube charged with silver cyanide (20 g) and glass wool. The reaction tube became warm and the rate of flow of silyl iodide was controlled to avoid over-heating. A little hydrogen was formed. Unreacted silyl iodide was distilled off from the silyl *iso*-cyanide at −78°, and re-passed through a fresh amount of silver cyanide. A total of 0·9270 g of silyl *iso*-cyanide was obtained. The material (0·1401 g) was analysed by hydrolysis with 30 per cent sodium hydroxide solution. Hydrogen evolved was measured. The cyanide in the hydrolysate was determined by LIEBEG's method.[8] Silicon was determined by hydrolysing another sample (0·1129 g), acidifying the hydrolysate strongly with hydrochloric acid, and weighing as silica. (Found: H 5·24, Si 49·5, CN 45·2, per cent M 57·5 SiH_3NC requires H 5·26, Si 49·1, CN 45·6, per cent M 57·0).

Reaction of Silyl Iodide with Mercuric Cyanide

The reaction was studied as in the previous experiment, using 0·7 g of silyl iodide and 12 g of mercuric cyanide. No reaction took place at room temperature, but when the reaction tube was warmed gently with a smoky coal-gas flame, reaction ensued. No hydrogen was evolved. Silyl *iso*-cyanide was found to be present in the middle fraction to distil from a bath at −46°. It was identified by its distillation properties and by its melting point (33°).

Decomposition of Silyl iso-Cyanide

Small amounts (0·06 to 0·1 g) of silyl *iso*-cyanide were sealed in small tubes *in vacuo*. Large amounts of solid phase were present. Some samples showed a faint black band of condensed mercury vapour. The pure samples remained colourless for approximately six months, and then a dark brown solid film began to form evenly over the entire inside surface of the tubes. The mercury-contaminated samples decomposed much more rapidly. No hydrogen was found to be present after opening a tube of absolutely pure silyl *iso*-cyanide after a period of twenty months. Substances present were unchanged silyl *iso*-cyanide (0·0112 g; M (found) 58·2, (calcd.) 57·0; vapour pressure at 0·0° (found)

[8] VOGEL, *Quantitative Inorganic Analysis*, Longmans, Green & Co., London, 1946, page 327.

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4·23 cm, (calcd.) 4·14 cm), silane (0·0264 g; *M* (found) 32·1, (calcd.) 32·0), and a non-volatile brown solid which gave off much hydrogen on hydrolysis with aqueous alkali (Si—H and/or Si—Si bonds present). The hydrolysate gave very strong tests for cyanide ion.

Hydrolysis of Silyl iso-*Cyanide*

Silyl *iso*-cyanide (0·1370 g) was distilled into an evacuated tube immersed in liquid nitrogen together with 0·5 ml of degassed distilled water. The tube was sealed off and was allowed to warm up to room temperature. Reaction occurred instantaneously, and after five minutes the tube was opened, and volatile material removed. No hydrogen was present and no residue remained in the tube. The products other than unchanged water were, disilyl ether (0·0940 g; M (found) 78·2, (calcd.) 78·0; Vapour pressures (found) 6·27 cm at −64·0°, 9·39 cm at −57·8°, 11·1 cm at −55·0°. Literature values[9] are 5·8 cm at −65°, 8·1 cm at −60°, 10·9 cm at −55°), and hydrogen cyanide (0·0650 g; M (found) 27·2, (calcd.) 27·0; Vapour pressure at 0·0° (found) 26·25 cm. Literature value[10] at −0·1° is 26·4 cm). The yields of both the disilyl ether and hydrogen cyanide were 100·2 per cent of the theoretical.

Reaction of Silyl iso-*Cyanide with Silver Chloride*

The reaction was studied by streaming the vapour of silyl *iso*-cyanide (0·2246 g) through a horizontal tube charged with silver chloride (15 g) and glass wool. The *iso*-cyanide was passed through the tube twice. No reaction appeared to occur. Substances recovered from the reaction were silyl *iso*-cyanide (0·2157 g; vapour pressure at 0·0° (found) 4·21 cm, (calcd.) 4·14 cm), which corresponded to a 90 per cent recovery, and an unidentified material (0·0058 g) which had distillation properties consistent with silyl chloride, SiH_3Cl, but which could not be identified further because of the very small amount of material available.

PRODUCTION AND REACTIONS OF SILYL *ISO*-THIOCYANATE

Reaction of Silyl Iodide with Silver Thiocyanate

The silver thiocyanate was formed by precipitation from silver nitrate and potassium thiocyanate. The reaction was studied by streaming the vapour of silyl iodide (1·1560 g) through a horizontal tube charged with silver thiocyanate (20 g) and glass wool. The reaction proceeded extremely vigorously, with the evolution of much heat and hydrogen if the rate of passage of the silyl iodide was too great: consequently the rate of flow of silyl iodide was controlled to avoid over-heating and decomposition. Silyl *iso*-thiocyanate (0·4340 g) was found to be present amongst the products of the reaction in a fraction which condensed in a trap at −64°. Small amounts of thiocyanic acid were also formed and passed through the −64° trap, and then immediately polymerized on warming to room temperature. The silyl *iso*-thiocyanate (0·1152 g) was analysed by hydrolysis with 30 per cent sodium hydroxide solution. Hydrogen evolved was measured. The thiocyanate in the hydrolysate was determined by the addition of excess standard silver nitrate solution followed by back titration with standard potassium thiocyanate. Silicon was determined by hydrolysing another sample (0·1564 g), acidifying the hydrolysate strongly with hydrochloric acid, and weighing as silica. (Found: H 3·36, Si 31·35, CNS 65·1, per cent *M* 89·5. SiH_3NCS requires H 3·37, Si 31·45, CNS 65·2; per cent M 89·0).

Decomposition of Silyl iso-*Thiocyanate*

Silyl *iso*-thiocyanate (0·1214 g) was sealed in a 12-ml tube *in vacuo* and was stored for twelve days at room temperature. A large liquid phase was present at all times. When the tube was opened, 2·4 cc hydrogen at N.T.P. were present. This was equivalent to 7·1 per cent of the hydrogen in that portion of the sample which had decomposed. Substances recovered were unchanged silyl *iso*-thiocyanate (0·0316 g or 26 per cent recovery; M (found) 89·9, (calcd.) 89·0; Vapour pressure at 0·0° (found) 1·63 cm, (calcd.) 1·60 cm), and monosilane (0·0011 g; M (found) 28·5, (calcd.) 32·0); the latter compound gave no test for sulphide ions on hydrolysis, and was not, therefore, hydrogen sulphide. Small amounts of two high-boiling-point unidentifiable liquids were also obtained. A

[9] Stock, Somieski, and Wintgen, *Ber.*, **50**, 1754, (1917).
[10] Perry and Porter, *J. Amer. Chem. Soc.*, **48**, 299, (1926).

white solid which was not sulphur remained in the storage tube. It dissolved in potassium hydroxide solution with little evolution of hydrogen. The solution gave strong reactions to tests for thiocyanate and cyanide ions. Therefore it appears that the solid was probably complex polymerized thiocyanic acid derivatives.

Hydrolysis of Silyl iso-*Thiocyanate*

Silyl *iso*-thiocyanate (0·1238 g) was distilled into an evacuated tube immersed in liquid nitrogen together with 0·5 ml of degassed distilled water. The tube was sealed off and allowed to warm up to room temperature. Reaction occurred as soon as the compound began to melt, and appeared to be complete by the time it had reached room temperature. After five to ten minutes the tube was opened, and 16·9 cc of hydrogen at N.T.P. were found to be present. The volatile material was removed, and a white powder remained in the hydrolysis vessel. The products, other than unchanged water, were disilyl ether (0·0252 g; M (found) 77·5, (calcd.) 78·0; vapour pressures (found) 5·77 cm at −64·5°, 8·78 cm at −58·0°. Literature values[10] are 5·8 cm at −65°, 8·1 cm at −60°, 10·9 cm at −55°), and thiocyanic acid (0·0142 g; M (found) 54·0, (calcd.) 59·0). The latter compound was also identified by the fact that it decomposed especially in the presence of water to give xanthine hydride, the white solid remaining in the hydrolysis vessel, and hydrogen cyanide.[11] The traces of hydrogen cyanide present would account for the lowering of the molecular weight of the thiocyanic acid from which it could not be separated by distillation. The yield of disilyl ether was 46·5 per cent of the theoretical.

Reaction between Silyl iso-*Thiocyanate and Silver Cyanate*

See next section.

ATTEMPTED PREPARATIONS OF SILYL CYANATE

Reaction between Silyl Iodide and Silver Cyanate

Silver cyanate was prepared by precipitation from silver nitrate and potassium cyanate. The reaction was studied by streaming the vapour of silyl iodide (0·3902 g) through a horizontal tube charged with silver cyanate (15 g) and glass wool. The reaction tube became warm and the rate of flow of silyl iodide was controlled to avoid over-heating. A little hydrogen was formed. The products isolated were cyanic acid (0·15 g; M (found) 43·0, (calcd.) 43·0; boiling-point (found) 24·0°. Literature value[12] is 23·6°), and silicon tetra-*iso*-cyanate (0·40 g; melting-point (found) 26·0–26·3°. Literature value[12] is 26 ± 0·5°). The identity of the latter compound was checked by hydrolysing it in aqueous alkali. No hydrogen was evolved (indicating the absence of Si—H or Si—Si bonds) and the hydrolysate gave excellent qualitative tests for the cyanate ion. The contents of the reaction tube had changed to a deep black colour, indicating the probable presence of finely-divided metallic silver.

The Reaction between Silyl Iodide and Potassium Cyanate

The reaction was studied by placing silyl iodide (0·5235 g) and potassium cyanate (0·25 g) in a 250-ml reaction vessel, which was sealed and left at room temperature for twelve days. Some liquid silyl iodide was present at all times. No hydrogen was evolved, and an almost quantitative recovery of silyl iodide (*M* (found) 156·0, (calcd.) 158·0) was obtained.

Reaction between Silyl iso-*Thiocyanate and Silver Cyanate*

The reaction was studied by streaming the vapour of silyl *iso*-thiocyanate (0·1434 g) through a horizontal tube charged with silver cyanate (15 g) and glass wool. The reaction tube became warm and the rate of flow was controlled to avoid over-heating. A little hydrogen was evolved. The substances isolated were cyanic acid (0·0445 g; M (found) 44·3, (calcd.) 43·0; boiling-point (found) 21·3°, Literature value[12] is 23·6°), and silicon tetra-*iso*-cyanate (0·0762 g); the identity of the latter compound was gained from its distillation properties in the vacuum system, and from the fact that, when it was hydrolysed in aqueous alkali, very little hydrogen was evolved (indicating the absence of Si—H and/or Si—Si bonds). The hydrolysate gave strong tests for cyanate ion. An unidentified compound

[11] LINNARD, *Z. anorg. Chem.*, **236**, 200, (1938).
[12] FORBES and ANDERSON, *J. Amer. Chem. Soc.*, **62**, 761, (1940).
[13] WILLIAMS, *Cyanogen Compounds*. Edward Arnold & Co., London, 1948, page 308.

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(0·1016 g; *M* 44·6), which passed through a −134° bath, was also obtained. When hydrolysed, hydrogen was evolved (indicating the presence of Si—H bonds), and the hydrolysate gave no positive test for sulphide ions.

INFRA-RED ABSORPTION SPECTRA

A Perkin-Elmer model 21 double-beam recording I-R spectrophotometer with a sodium chloride optical system was used. "Glyptal" cement was used to hold the 5-mm sodium chloride end-plates in position on the 10-cm gas cell.

With silyl *iso*-cyanide, pressures of 8·67 cm, 1·00 cm, and 0·13 cm were used. Measurements on silyl *iso*-thiocyanate were carried out at pressures of 3·18 cm, 0·5 cm, and 0·075 cm. During the measurement at the highest pressure a minute amount of hydrogen was formed.

The silyl *iso*-cyanide spectrum indicates that the compound is of the symmetric top type. Silyl *iso*-thiocyanate is also a symmetric top molecule, and is discussed more fully in another paper.[7] Several of the fundamental absorption bands of both compounds are listed below:

Vibration	SiH_3NC cm^{-1}	SiH_3NCS cm^{-1}
Si—H stretch	2208 (s) overtone 1613 (w) overtone 1890 (w) overtone 3125 (m)	2198 (s) overtone 1905 (m) overtone 3145 (w)
SiH_3 deformation (i.e., SiH_3 bend)	914 (s); 923 (s); 929 (s) Probable overtone 1351 (m) Probable overtone 1370 (m)	946 (s); 952 (s) Probable overtone 1414 (m) Probable overtone 1420 (m)
SiH_3 rock + unidentified bands	691 (s), 689 (s) Broad bands	696 (s), 721 (s) Broad bands—possibly with CS or CN vibration
NCS stretch[14, 15]		2045 (s); 2096 (s)
Unidentified	1166 (w) 2033 (w) 2433 (w)	1031 (s) 1038 (s) 1094 (m) possibly disilyl ether impurity 1661 (w) 2538 (m) 2597 (s) 2646 (m) 3521 (w) 4082 (w)

w = weak m = moderate s = strong

Acknowledgements—The author wishes to express his thanks to Professor H. J. EMELÉUS and to Dr. A. G. MADDOCK for advice and many helpful discussions during the period of research. He is also indebted to the Shell Petroleum Company Ltd. for a postgraduate research fellowship.

[14] GORDY and WILLIAMS, *J. Chem. Phys.*, **4**, 85, (1936).
[15] KAHOVEC and KOHLRAUSCH. *Z. phys. Chem.*, **B37**, 421, (1937).

J. Inorganic and Nuclear Chemistry, 1956, Vol. 2, pp. 95–113. Pergamon Press Ltd., London

ON MANGANESE CYCLOPENTADIENIDE AND SOME CHEMICAL REACTIONS OF NEUTRAL *BIS*-CYCLOPENTADIENYL METAL COMPOUNDS

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(*Received* 8 *April* 1955)

Abstract—The compound $(C_5H_5)_2Mn$ has been prepared by the reaction of the manganous halides with C_5H_5Na in tetrahydrofuran solution; the chemical and physical properties are described.

The magnetic susceptibility of $(C_5H_5)_2Mn$ has been measured over the range 77° to 530°K; it shows antiferromagnetic behaviour with a Néel temperature of 134°K, and there is a sharp susceptibility and colour transition at 432°K associated with complete destruction of co-operative phenomena existing in the crystal, which undergoes a change in structure at this point. The compound is shown to be ionic in nature by magnetic studies and by other physical and chemical evidence.

Magnesium cyclopentadienide $(C_5H_5)_2Mg$ is described, and improved preparative methods for $(C_5H_5)_2V$, $(C_5H_5)_2Cr$, $(C_5H_5)_2Co$, and $(C_5H_5)_2Fe$ are given.

The chemical reactivities of the $(C_5H_5)_2M$ compounds of V, Cr, Mn, Fe, Co, Ni, and Mg, and of C_5H_5Na are compared, and evidence for ionic behaviour of $(C_5H_5)_2V$ and $(C_5H_5)_2Cr$ is discussed.

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1. INTRODUCTION

IN a preliminary note[1] the preparation of the compounds $(C_5H_5)_2Mn$ and $(C_5H_5)_2Mg$ were reported. This paper presents details of the preparations and of the physical and chemical properties of these compounds. The manganese compound has subsequently been prepared by a procedure different from the one described here.[2]

In contrast to the neutral *bis*-cyclopentadienyl metal compounds of titanium,[3] vanadium,[4] chromium,[5] iron[6] cobalt,[6] and nickel,[6] in which the cyclopentadienyl rings are bound to the metal atom by a unique semidelocalized two-electron covalent bond,[7, 8, 9] the present work shows that in $(C_5H_5)_2Mn$ the metal-to-ring bonds are electrostatic in nature.

The acidity of cyclopentadiene[10] was first recognized by THIELE,[11] and metal derivatives of the anion, e.g., C_5H_5K[12] and C_5H_5MgBr,[13] have long been known.

[1] G. WILKINSON and F. A. COTTON, *Chemistry and Industry*, **11**, 307 (1954).
[2] E. O. FISCHER and R. JIRA, *Zeit. f. Naturforschg.*, **9b**, 618 (1954).
[3] (a) G. WILKINSON and J. M. BIRMINGHAM, *J. Amer. Chem. Soc.*, **76**, 4281 (1954). (b) A. K. FISCHER and G. WILKINSON (to be published).
[4] E. O. FISCHER and W. HAFNER, *Zeit. f. Naturforschg.*, **9b**, 503 (1954).
[5] G. WILKINSON, *J. Amer. Chem. Soc.*, **76**, 209 (1954).
[6] G. WILKINSON, P. L. PAUSON, and F. A. COTTON, *J. Amer. Chem. Soc.*, **76**, 1970 (1954).
[7] W. MOFFITT, *J. Amer. Chem. Soc.*, **76**, 3386 (1954).
[8] J. D. DUNITZ and L. E. ORGEL, *Nature*, **171**, 121 (1953), have referred to *bis-cyclopentadienyliron* (ferrocene), $(C_5H_5)_2Fe$, as a "molecular sandwich," and we now refer to the type of metal-to-ring bond in this compound as a "sandwich bond."
[9] J. D. DUNITZ and L. E. ORGEL, *J. Chem. Phys.*, **23**, 954 (1955).
[10] N. VON E. DOERING and L. H. KNOX, *J. Amer. Chem. Soc.*, **76**, 6210 (1954), quote a report that potassium *t*-butoxide (pK_a 19) converts cyclopentadiene quantitatively into the potassium salt. Other estimates (G. W. WHELAND, *J. Chem. Phys.*, **2**, 474 (1934)) indicate that the pK for cyclopentadiene is somewhat lower than the minimum value of 21 for indene (W. K. MCEWEN, *J. Amer. Chem. Soc.*, 4756 (1952)).
[11] J. THIELE, *Ber.*, **33**, 666 (1900).
[12] J. THIELE, *Ber.*, **34**, 68 (1901).
[13] V. GRIGNARD and C. COURTANT, *Compt. Rend.*, **158**, 1763 (1914).

It has only recently been pointed out, however, that electropositive elements in general may be expected to form salts of the $C_5H_5^-$ ion, and ionic derivatives of scandium, yttrium, lanthanum, and several rare-earth elements of the formula $(C_5H_5)_3M$ have been described.[14] Whilst the magnesium compound, $(C_5H_5)_2Mg$, may be expected to be ionic in nature, manganese is not a highly electropositive element, and the formation of an ionically bonded $(C_5H_5)_2Mn$ compound must be attributed to the stability of the manganous ion.

2. THE NATURE OF THE BONDING IN $(C_5H_5)_2Mn$

The evidence for the ionic nature of the metal-to-ring bonds in $(C_5H_5)_2Mn$ is now presented. In view of this evidence, the manganese compound is perhaps best designated as manganese(II) cyclopentadienide.[15]

A. *Magnetic Properties*

For a "sandwich bonded" manganese compound $(C_5H_5)_2Mn$, the molecular orbital theory of bonding,[7, 8, 9] which requires the use of two d orbitals of the metal in metal-to-ring bonding, sets the maximum number of unpaired electrons as three. The considerations of MOFFITT[7] regarding the mixing and splitting of the d_z and s levels of the metal atom lead to the possibility of only one unpaired electron.

The magnetic behaviour of $(C_5H_5)_2Mn$ is anomalous, and is not in accord with the predictions for a "sandwich bonded" molecule. Representative data is presented in Figs. 1 and 2 and in Table 2 in the experimental section. In the range 67° to 432°K, $(C_5H_5)_2Mn$ shows antiferromagnetic behaviour characteristic of some other manganous salts. The Néel temperature is 134 ± 2°K; between 200° and 420°K a plot of $1/\chi$ *vs* T yields the values $c = 6{\cdot}43$ and $\theta = -492$°K in the Curie-Weiss equation $\chi = c/(T - \theta)$. In Table 1 these data are compared with the corresponding data for some other antiferromagnetic manganous salts.

TABLE 1

Compound	Néel temperature	Weiss constant, θ	θ/T_c
$Mn(C_5H_5)_2$	134°K	−492°K	−4·03
MnO*	122	−610	−5·0
MnS*	165	−528	−3·2
MnF_2*	72	−113	−1·57

* Data taken from reference (16).

[14] G. WILKINSON and J. M. BIRMINGHAM, *J. Amer. Chem. Soc.*, **76**, 6210 (1954), and *J. Amer. Chem. Soc.* (in press)

[15] We have previously[1] referred to $(C_5H_5)_2Mn$ and $(C_5H_5)_2Mg$ as "dicyclopentadienyl" compounds in order to distinguish them from the chemically dissimilar *bis*-cyclopentadienyl metal compounds of the ferrocene type, and we also used in this context the term "alkyl type." The latter term has led to misinterpretation (E. O. FISCHER, *Z. Naturforschg.*, **9b**, 619 (1954)). In view of the stability of the C_5H_5-anion and the characterization of numerous ionic metal derivatives, we adopt the term "cyclopentadienide" for them. Thus C_5H_5Na is termed sodium cyclopentadienide rather than cyclopentadienylsodium following the customary nomenclature for organometallic compounds. This use of "cyclopentadienide" falls in line with the established usage, e.g., of "acetylide," for metal salts of acidic hydrocarbons. The use of the prefix "di-" has an additional connotative disadvantage in that these metal derivatives have no direct connection with dicyclopentadiene.

Manganese cyclopentadienide differs in its magnetic behaviour from other antiferromagnetic manganous salts and from other antiferromagnetic materials in general. The most unusual aspect of its behaviour is the sharp discontinuity at

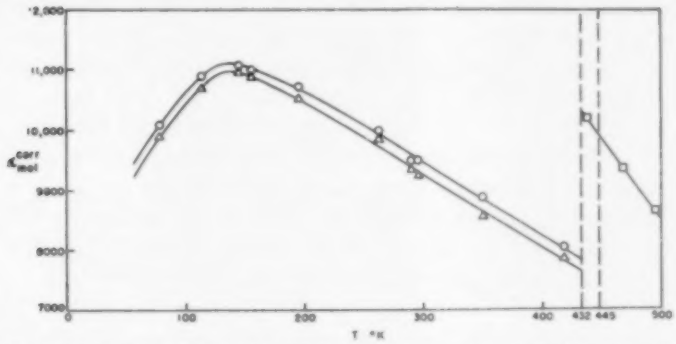

FIG. 1.—Magnetic susceptibility of crystalline manganese cyclopentadienide. ○ at 6050 gauss, △ at 2600 gauss. □ high-temperature form and melt averaged over all fields.

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432°K, which is associated also with a change in colour from the amber-brown of the low temperature form of $(C_5H_5)_2Mn$ to the pale pink of the solid form which is stable between the transition temperature and the melting-point at 446°K. The magnetic susceptibility of the brown form is dependent upon field strength, although

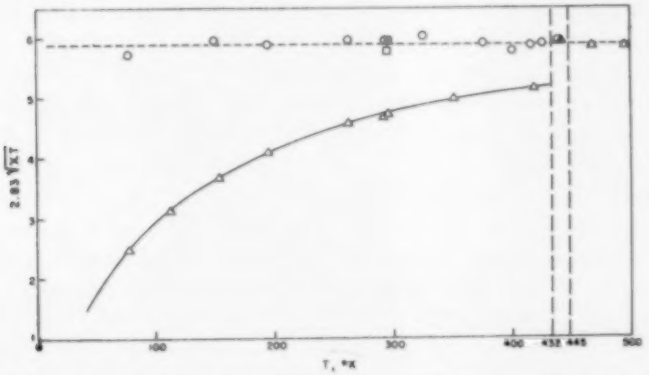

FIG. 2.—Magnetic susceptibility of pure $(C_5H_5)_2Mn$ at 6050 gauss, △. A dilute solid solution of $(C_5H_5)_2Mn$ in $(C_5H_5)_2Mg$, ○, and solutions of $(C_5H_5)_2Mn$ in organic solvents, □ (averaged over all fields).

not strongly so, both below and above the Néel temperature; in other antiferromagnetic substances field-strength dependence tends to fall off above the Néel temperature. Finally, although with other antiferromagnetic salts the Curie constant, c, can be used to calculate a value of effective magnetic moment, μ_{eff}, which agrees with that expected from the values of spin and orbital angular momenta for the metal atom,[16] this is not the case with $(C_5H_5)_2Mn$. For the Mn^{++} ion in an S state, the spin-only value of 5·92 B.M. should be obtained, whereas $\mu_{eff} = 2{\cdot}83\sqrt{c} = 7{\cdot}18$ B.M.

These observations indicate that while spin coupling between neighbouring

[16] C. KITTEL, *Introduction to Solid State Physics*, John Wiley & Sons, New York (1953), p. 189.

manganese atoms in the crystal of $(C_5H_5)_2Mn$ breaks down to a considerable extent at the Néel temperature, some form of co-operative interaction persists until the second, discontinuous transition at 432°K.

In the absence of detailed structural knowledge, little can be said quantitatively regarding the magnetic anomalies. The 432°K transition must be associated with complete removal of co-operative phenomena, and is a result of a lattice reorganization. It may be noted that observations on single crystals with a hot-stage microscope indicate a change in crystal form at 432°K. Observation of the dichroism of a crystal of brown $(C_5H_5)_2Mn$ before the transition and after cooling subsequent to it also indicates destruction of the original crystal lattice of the brown form.

The pink form of $(C_5H_5)_2Mn$, which is stable from 432° to 445°K, has a molar susceptibility of $+10{,}250 \times 10^{-6}$ c.g.s.u., which corresponds to a μ_{eff} of 5·9 B.M., assuming $\theta = 0$. The liquid shows $\mu_{eff} = 5{\cdot}9$ B.M., and follows the Curie law ($\theta = 0$) up to at least 530°K.

We have studied also the effect of dilution upon the magnetic behaviour of $(C_5H_5)_2Mn$. Dilute solutions in benzene and ether at room temperature were found to have effective magnetic moments of ~5·8 B.M. according to the equation $\mu_{eff} = 2{\cdot}83\sqrt{\chi_{mol}^{corr}\,T}$. The manganese and magnesium cyclopentadienides form mixed crystals with the maximum attainable content of $(C_5H_5)_2Mn$, being 40–50 per cent. The concentrated manganese solutions are yellow-orange, and with increasing dilution below 10 per cent $(C_5H_5)_2Mn$ assume the pale pink colour characteristic of the high-temperature form of pure $(C_5H_5)_2Mn$ and of the manganous ion. We have measured the magnetic susceptibility of a dilute solid solution containing 8·06 mole per cent $(C_5H_5)_2Mn$ in $(C_5H_5)_2Mg$ from 77° to 438°K. Over the entire temperature range the susceptibility of the manganese cyclopentadienide now follows Curie's law, having $\mu_{eff} = 5{\cdot}94 \pm 0{\cdot}05$ B.M. There is no discontinuity at any temperature in this range.

The magnetic data in themselves provide compelling evidence that the metal-to-ring binding in $(C_5H_5)_2Mn$ is due to electrostatic forces between the Mn^{++} and $C_5H_5^-$ ions. The presence of five unpaired electrons in the dilute samples, in the pink form, and in the melt cannot be reconciled with any energy-level scheme for a "sandwich bonded" $(C_5H_5)_2Mn$ molecule. The antiferromagnetic behaviour of pure $(C_5H_5)_2Mn$ is not unexpected, in view of the similar behaviour of other ionic manganous compounds.

B. *Mass Spectra*

Mass spectrometer studies[17] of $(C_5H_5)_2M$ compounds clearly show the difference between the "sandwich bonded" molecules of V, Cr, Fe, Co, Ni, and Ru on the one hand, and the manganese and magnesium compounds on the other. Not only are the relative yields of the main ions $C_{10}H_{10}M^+$, $C_5H_5M^+$, and M^+, quite different for the two groups, the most abundant species being $C_{10}H_{10}M^+$ for the "sandwich bonded" molecules, and $C_5H_5M^+$ for the manganese and magnesium compounds, but the latter also differ in showing abundant ions of lower mass. Whilst not conclusive in themselves, these observations provide evidence that $(C_5H_5)_2Mn$ and $(C_5H_5)_2Mg$ closely resemble each other and differ noticeably from the cyclopentadienyl compounds of other transitional metals.

[17] L. FRIEDMAN, A. P. IRSA, and G. WILKINSON, *J. Amer. Chem. Soc.*, 77, 3689 (1955).

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C. *Infra-red Absorption Measurements*

The chemical reactivity of $(C_5H_5)_2Mn$ and $(C_5H_5)_2Mg$ complicates the study of their infra-red absorption spectra. Both compounds are rather sparingly soluble in, and react with, carbon tetrachloride. With carbon disulphide, $(C_5H_5)_2Mg$ reacts instantaneously, while $(C_5H_5)_2Mn$, which reacts slowly with the solvent, has a solubility so low that only the strong bonds at ~1000 and 760 cm^{-1} can be observed.

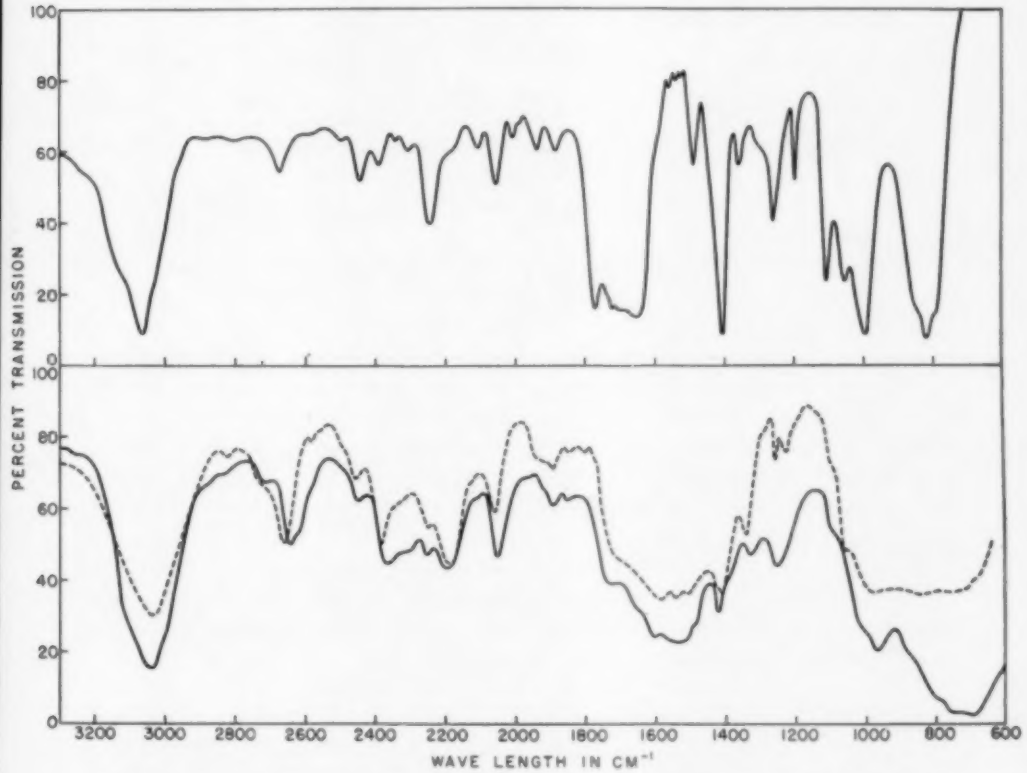

FIG. 3.—Infra-red spectra of single crystals of ferrocene (top), and manganese (broken line), and magnesium (full line) cyclopentadienides.

In order to obtain spectra over a wider range than is possible using unreactive solvents, the infra-red spectra of single crystals of $(C_5H_5)_2Fe$, $(C_5H_5)_2Mn$, and $(C_5H_5)_2Mg$ were measured, using a microscope attachment. The spectra (Fig. 3) of $(C_5H_5)_2Mn$ and $(C_5H_5)_2Mg$ closely resemble each other, and differ appreciably from the ferrocene spectrum. The main difference here is the lower intensity in the manganese and magnesium compounds of the band in the 1410-cm^{-1} region, which in the case of ferrocene has been assigned[18] to a C—C ring breathing mode. This difference is in accord with the increased olefinic nature of the C_5H_5 anion compared to the C_5H_5 ring in ferrocene. The bands in the C—H stretching region in each compound can be resolved into three components, in the manganese case for example at 3150, 3105, and 3060 cm^{-1}; since a single C—H stretching frequency is to be

[18] E. R. LIPPINCOTT and R. D. NELSON, *J. Chem. Phys.*, **21**, 1307 (1953).

expected for the C_5H_5 ring either in ferrocene or in the symmetrical C_5H_5 anion, the splittings must be attributed to interaction between adjacent groups in the crystal. The ring both in ferrocene and the ion must be expected to have some common features in the infra-red spectrum, and it may be noted that in cyclohexane solution there are strong bands at 1000 and 760 cm^{-1} in both $(C_5H_5)_2Mn$ and $(C_5H_5)_2Mg$ similar to the bands in ferrocene.

D. *Chemical and Ionic Properties*

For all $(C_5H_5)_2M$ compounds, an ionic dissociation reaction

$$(C_5H_5)_2M \rightleftharpoons (C_5H_5)M^+ + C_5H_5^- \rightleftharpoons M^{++} + 2C_5H_5^- \qquad (1)$$

is theoretically possible. Unless this dissociation is exceedingly small or is extremely slow, i.e., the C_5H_5-metal bonds are to be considered formally covalent, two types of chemical reactions, which are actually related to each other, should be shown by the $(C_5H_5)_2M$ compounds.

Firstly, cationic exchange reactions between $(C_5H_5)_2M$ and M^{++}, or between $(C_5H_5)_2M$ and another doubly charged cationic species, should occur at a measurable rate; also, agents forming strong complexes may remove the metal ion from the compound. Secondly, even if the dissociation is very small, providing the equilibrium is labile, the compounds should undergo reactions which are typical for the cyclopentadienide ion. In addition, if the C_5H_5-metal bonds are considerably ionic in nature, lowered solubility of $(C_5H_5)_2M$ compounds in solvents of low dielectric constant may be expected; if the dissociation is appreciable, conducting solutions may be formed in solvents of high dielectric constant, where the metal ions may become solvated.

Comparing the behaviour of the $(C_5H_5)_2M$ compounds of V, Cr, Mn, Fe, Co, Ni, and Mg and of C_5H_5Na, with regard to the above considerations, we have found that several reactions allow valuable information concerning the nature of the metal to ring bond to be obtained.

(a) *Exchange Reactions*

The only isotopic exchange reaction studied so far is that between ferrocene and the ferrous ion in an aqueous ethanolic medium. We have been unable to detect any exchange over a period of twelve months. In the absence of such information, the results of metathetical exchange reactions between $(C_5H_5)_2M$ compounds and ferrous chloride are of importance.

The reactions of ferrous chloride, and indeed of other metal halides, with C_5H_5Na and C_5H_5MgBr (and $(C_5H_5)_2Mg$), are rapid and complete and, of course, are well established preparative methods for compounds of the type $[(C_5H_5)_2M^n]X_{n-2}$. The $(C_5H_5)_2M$ compounds of Co and Ni yield no trace of ferrocene even on refluxing with ferrous chloride in tetrahydrofuran solution for several hours. $(C_5H_5)_2V$ forms an indigo solution of $(C_5H_5)_2VCl$ and only a faint trace of ferrocene; $(C_5H_5)_2Co$ is similarly oxidized to cobalticinium chloride; metallic iron is formed in these reactions. $(C_5H_5)_2Ni$ does not react at all.

By contrast, $(C_5H_5)_2Mn$ reacts instantaneously and quantitatively with ferrous chloride at 25°C to give ferrocene and manganous chloride. $(C_5H_5)_2Cr$ also reacts instantaneously, but yields of ferrocene exceeding 70 per cent of the theoretical have

not been obtained, and in addition a blue-green compound, not yet completely characterized but which is believed to have only one C_5H_5 ring per metal atom, is formed.

(b) *Reactions Directly Indicating the Presence of the $C_5H_5^-$ Ion*

1. *Water.* Cyclopentadiene is a very weak acid, hence even slight dissociation according to the equation (1) should make possible reaction with water to form cyclopentadiene and metal hydroxide. Such a reaction will be favoured by an increase in hydrogen-ion concentration. A $(C_5H_5)_2M$ compound which is wholly or even partially ionic in the crystal, may be expected to be hydrolyzed by water. The reactions of the various compounds with water and dilute acids are tabulated below.

Compound	Result of treatment with		
	H_2O	3N HCl	3-4N HNO_3
C_5H_5Na	instant. hydrolysis	instant. hydrolysis	instant. hydrolysis
$(C_5H_5)_2Mg$	instant. hydrolysis	instant. hydrolysis	instant. hydrolysis
$(C_5H_5)_2V$	no reaction	little or no observable reaction	ready oxidation to $[(C_5H_5)_2V]^{++}$
$(C_5H_5)_2Cr$	no reaction	hydrolysis and oxidation	hydrolysis and oxidative decomposition
$(C_5H_5)_2Mn$	instant. hydrolysis	instant. hydrolysis	instant. hydrolysis
$(C_5H_5)_2Fe$	no reaction	no reaction	oxidation to $[(C_5H_5)_2Fe]^+$
$(C_5H_5)_2Co$	very slow oxidation to $[(C_5H_5)_2Co]^+$	oxidation	oxidation
$(C_5H_5)_2Ni$	no reaction	no reaction	oxidation to $[(C_5H_5)_2Ni]^+$

It may be seen that no hydrolytic reaction occurs with the $(C_5H_5)_2M$ derivatives of V (traces of cyclopentadiene have been detected by infra-red measurements after solvent extraction), Fe, Co, and Ni. The sodium, magnesium, and manganese compounds hydrolyze under all conditions. $(C_5H_5)_2Cr$ is not affected by water, but is partially hydrolyzed[5] and partially oxidized in acid solution.

2. *Aldehydes, ketones, and dienophiles.* It is well known that $C_5H_5Na(K)$ and C_5H_5MgBr react with a variety of aldehydes and ketones, yielding on hydrolysis fulvene derivatives which are often highly coloured.[11, 13] It has also been observed that ferrocene does not react with maleic anhydride in boiling benzene,[19] whilst the silicon cyclopentadienyl derivatives do so,[20] and the $C_5H_5^-$ ion also reacts.

We have tested the $(C_5H_5)_2M$ compounds with benzophenone, *m*-nitrobenzaldehyde, maleic anhydride, and methyl maleate. These reactions do not provide unambiguous evidence concerning ionic character; while *only ferrocene* (and also ruthenocene) fails to react with *all* of these reagents, the possibility of various modes of reaction makes interpretation impossible until the reaction products are characterized. More detailed studies of some of these reactions are in progress, but some qualitative observations are of interest.

[19] R. B. Woodward, M. Rosenblum, and M. C. Whiting, *J. Amer. Chem. Soc.*, **74**, 3458 (1952).
[20] K. C. Frisch, *J. Amer. Chem. Soc.*, **75**, 6050 (1953).

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With benzophenone, C_5H_5Na, $(C_5H_5)_2Mg$, and $(C_5H_5)_2Mn$ lead unequivocally to the red diphenylfulvene; $(C_5H_5)_2V$, $(C_5H_5)_2Cr$, and $(C_5H_5)_2Co$ gave coloured reaction products with benzophenone, whilst $(C_5H_5)_2Fe$ and $(C_5H_5)_2Ni$ did not react. With the aldehyde only $(C_5H_5)_2Fe$ failed to react.

With maleic anhydride C_5H_5Na, $(C_5H_5)_2Mg$, and $(C_5H_5)_2Mn$ give similar orange-red benzene insoluble adducts. The $(C_5H_5)_2M$ compounds of V, Cr, Co, and Ni also react in an as yet undetermined way. However, it should not be concluded that these compounds are necessarily polyolefinic or ionic in nature, since reaction mechanisms other than the Diels-Alder reaction are possible. Thus the $(C_5H_5)_2M$ compound may act as a strong reducing agent, and there is also the possibility of uncatalyzed Friedel-Crafts reaction as occurs with the pseudo-aromatic molecule, azulene. In the case of $(C_5H_5)_2Co$, the reaction product with maleic anhydride gives with water a yellow solution which has reactions of cobalticinium ion, showing that the "sandwich bonded" structure is still intact.

(c) *Solvation and Conductance Studies*

Solutions of the $(C_5H_5)_2M$ compounds and C_5H_5Na in liquid ammonia at −33°C and in tetrahydrofuran have been studied semiquantitatively. The results in liquid ammonia are summarized below:

Compound	Specific conductivity at −33°C	Remarks
C_5H_5Na	$1{\cdot}22 \times 10^{-3}$ ohm^{-1}	concentration: $5{\cdot}78 \times 10^{-3}$ M
$(C_5H_5)_2Mg$	$4{\cdot}5 \times 10^{-4}$ ohm^{-1}	concentration: $4{\cdot}67 \times 10^{-3}$ M
$(C_5H_5)_2Mn$	$1{\cdot}4 \times 10^{-5}$ ohm^{-1}	concentration: $1{\cdot}57 \times 10^{-3}$ M
$(C_5H_5)_2V$	$1{\cdot}1 \times 10^{-4}$ ohm^{-1}	Saturated solution Ammoniates formed
$(C_5H_5)_2Cr$	$4{\cdot}0 \times 10^{-4}$ ohm^{-1}	Saturated solution Ammoniates formed
$(C_5H_5)_2Fe$	Non-conducting	Slight solubility
$(C_5H_5)_2Co$	Non-conducting	Slight solubility
$(C_5H_5)_2Ni$	Non-conducting	Slight solubility

In liquid ammonia, the V, Cr, and Mn compounds give visible evidence of solvation; only the manganese compound has been analysed at the present time, but further studies on the ammonia systems are in progress. Ammoniates of $(C_5H_5)_2Mn$ with up to four ammonia molecules per manganese atom are formed. FISCHER[2] claimed the preparation of $[(NH_3)_6Mn](C_5H_5)_2$ by treatment of manganous thiocyanate with C_5H_5Na in liquid ammonia. The white material prepared by us containing four ammonia molecules was stable with respect to loss of ammonia in a vacuum of about one micron. Ammoniates of lower ammonia content are pale pink.

In liquid ammonia the deep purple $(C_5H_5)_2V$ becomes a pale lavender, appearing nearly white in thin layers. This substance is stable at room temperature in vacuum, but readily loses ammonia at 50–60°C, reverting completely to $(C_5H_5)_2V$.

The chromium compound forms several ammoniates. At −33°C in liquid ammonia the colour is pale blue; on removal of the liquid ammonia the solid at

−33°C turns lavender, and on pumping at room temperature it becomes a salmon-pink. At about 75°C all the ammonia is lost and the red $(C_5H_5)_2Cr$ is regenerated.

These ammoniates are quite different from the yellow $[(NH_3)_6Cr](C_5H_5)_2$ claimed by FISCHER,[21] which gave only traces of $(C_5H_5)_2Cr$ on thermal decomposition.

(d) Other Reactions

With carbon dioxide, C_5H_5Na and $(C_5H_5)_2Mg$ react very rapidly, $(C_5H_5)_2Mn$ rather slowly; on hydrolysis the dicarboxylic acid $(C_5H_5COOH)_2$ is formed.[12] With carbon disulphide, their behaviour is similar, and, in addition, the chromium, vanadium, and cobalt compounds react.

The ionic compounds also slowly react with chloroform; this reaction may proceed by ring expansion, as in the reaction of chloroform with sodium indenide.[22]

Alkyl and aryl halides are known to react with sodium or magnesium cyclopentadienide[23, 24] to form substituted cyclopentadienes. The $(C_5H_5)_2M$ compounds of V, Cr, Mn, Co also react with, for example, ethyl bromide; the reactions are being studied in detail. In the case of $(C_5H_5)_2Co$, the "sandwich bonded" structure is not destroyed, since cobalticinium bromide is formed; while, with $(C_5H_5)_2Cr$, blue crystals of empirical composition $C_{10}H_{10}Cr_2Br_2$ are formed.[25]

Several of the $(C_5H_5)_2M$ compounds react with carbon monoxide or nitric oxide to give diamagnetic products such as $C_5H_5V(CO)_4$,[4] $C_5H_5Mn(CO)_3$,[26, 2] $C_5H_5Co(CO)_2$,[26] C_5H_5NiNO,[26] and $(C_5H_5)_2Mn_2(NO)_3$;[27] these reactions are not indicative of ionic character, however.

Physical evidence for the ionic nature of $(C_5H_5)_2Mn$ in the crystal, the vapour phase, and in solution both in solvents and in $(C_5H_5)_2Mg$, has been presented above, and the magnetic evidence, particularly, is conclusive on this point. The chemical evidence also supports the thesis that $(C_5H_5)_2Mn$ is an ionically bonded compound. Thus the chemical behaviour of C_5H_5Na, $(C_5H_5)_2Mg$, and $(C_5H_5)_2Mn$ are strikingly similar, the reactions with water and with ferrous chloride being particularly notable and conclusive.

3. DISCUSSION

The most likely reason that manganese, although slightly more electropositive than adjacent chromium or iron, but far less so than other elements which give ionic cyclopentadienides, forms an ionic compound $(C_5H_5)_2Mn$, is to be found in the extra stability of divalent manganese as an ion. This stability of the Mn^{++} ion is a result of Hund stabilization, since the ion has a half-filled 3*d* shell (spectroscopic state $^6S_{5/2}$). There are many well-known chemical consequences of this fact, and this explanation has often previously been advanced in explaining the chemistry of the Mn(II) state—for example, the paucity of "inner orbital" or so-called "covalent" complexes of the ion. The manganese atom can form a metal-to-C_5H_5-ring bond of the "sandwich bond" type, provided the atom is not in the divalent state; such a bond has been shown to be present in the compound $C_5H_5Mn(CO)_3$,[26] in the ion $[(C_5H_5Mn(CO)_2NO]^+$,[26] and in the compound $(C_5H_5)_2Mn_2(NO)_3$ formed by the

[21] E. O. FISCHER and W. HAFNER, *Zeit. f. Naturforschg.*, **8b**, 217, 1327 (1953).
[22] W. E. PARHAM and M. E. REIFF, *J. Amer. Chem. Soc.*, **77**, 1177 (1955).
[23] K. ALDER and H. HOLZRICHTER, *Ann.*, **524**, 145 (1936).
[24] K. W. GREENLEE, Dissertation, Ohio State University, Columbus, Ohio, 1942: "Reactions of sodium derivative of unsaturated hydrocarbons."
[25] G. WILKINSON, L. T. REYNOLDS, and A. K. FISCHER (unpublished work).
[26] T. S. PIPER, F. A. COTTON, and G. WILKINSON, *J. Inorg. Nucl. Chem.*, **1**, 165 (1955).

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action of nitric oxide on manganese cyclopentadienide.[27] In the first two derivatives the manganese is univalent and the atom is then isoelectronic with Fe(II), which gives the "sandwich bonded" molecule ferrocene, $(C_5H_5)_2Fe$. It is noteworthy that, with Fe(III), which is isoelectronic with and often resembles Mn(II) in its properties, e.g., the heats of hydration of the ions,[28] the metal-to-ring bonds in the ferricinium ion $[(C_5H_5)_2Fe]^+$ are unquestionably of "sandwich bond" type; this is shown by the stability of the ion in solution, by the infra-red spectrum,[29] and by the fact that the ferrocene-ferricinium ion couple is a reversible one.[30] The different behaviour of Mn(II) and Fe(III) in their cyclopentadienyl derivatives may be due to the increased charge on the iron atom with a consequent increase in its polarizing power.

Although the present work allows unequivocal conclusions to be drawn regarding the bond type in $(C_5H_5)_2Mn$, no direct information on the configuration is provided. We have noted previously[14] that, in the $C_5H_5^-$ ion, the negative charge cannot be expected to be localized on a particular carbon atom, but that it will be distributed over the ion as a whole. In an ionic compound with a divalent cation, the two cyclopentadienide anions can be expected on electrostatic grounds to align themselves on opposite sides of the cation with their planes parallel. This structure is in fact exactly that appertaining in the "sandwich bonded" molecules such as ferrocene.[8] It is to be noted, however, that in the first case *the configuration is due merely to the geometry resulting from the charge distribution, where in the second it is a requirement of the metal-to-ring covalent bonding*. For an ionic compound of a univalent metal such as C_5H_5Na, the sodium atoms might be expected to be placed similarly between the parallel planes of the $C_5H_5^-$ anions in an infinite lattice structure. It is most interesting to note, therefore, that FISCHER[31] has recently found that $(C_5H_5)_2Mg$ indeed has a "sandwich" configuration in the crystal.* The reason for this, however, and the profound difference between the "sandwich bonded" molecules of the same stoichiometry and $(C_5H_5)_2Mg$ in other physical and chemical properties, appears to have been overlooked. The same criticism applies to $(C_5H_5)_2Mn$, which FISCHER[31] quotes as having a "sandwich" configuration.*

Since the manganous ion does not have a radius appreciably different from those of its neighbours in the first transitional series, the metal-to-ring distances to be expected in $(C_5H_5)_2Mn$ are only a little different from the distances in the $(C_5H_5)_2M$ compounds with "sandwich bonding." In the free state, in the vapour, in the melt, and in solution, $(C_5H_5)_2Mn$ will exist as an ionically bonded molecule—an "ion-triplet"—whose size is comparable to that of $(C_5H_5)_2Fe$. The similarity in melting-point, and of the vapour pressure and heat of vaporization of the liquid of $(C_5H_5)_2Mn$ and $(C_5H_5)_2Fe$, is in accord with this view. In the crystal, even, discrete molecules of $(C_5H_5)_2Mn$ may be expected. It should be noted, however, that while we find that $(C_5H_5)_2Mn$ and $(C_5H_5)_2Mg$ will form mixed crystals, $(C_5H_5)_2Fe$ and $(C_5H_5)_2Mn$

* *Note added in proof.*
Detailed X-ray diffraction studies of $(C_5H_5)_2Mg$ and $(C_5H_5)_2V$ have been given by E. WEISS and E. O. FISCHER [*Z. anorg. Chem.*, **278**, 219 (1955)] and a note by the same authors [*Z. Naturforschg.*, **10b**, 58 (1955)] gives data for $(C_5H_5)_2Mn$ showing the rhombic nature of the compound in the low temperature form and monoclinic nature in the high temperature form and in mixed crystals with $(C_5H_5)_2Mg$.

(27) T. S. PIPER and G. WILKINSON, *ibid.*, **2**, 38, (1956).
(28) L. E. ORGEL, *J. Chem. Soc.*, 4756 (1952).
(29) G. WILKINSON and J. M. BIRMINGHAM, *J. Amer. Chem. Soc.*, **76**, 4281 (1954).
(30) J. A. PAGE and G. WILKINSON, *J. Amer. Chem. Soc.*, **74**, 6149 (1952).
(31) E. O. FISCHER, *Zeit. f. Naturforschg.*, **9b**, 619 (1954).

will not do so. Although the heats of sublimation of solid $(C_5H_5)_2Mn$ and $(C_5H_5)_2Fe$ are very similar (17·3 and 16·8 kcal/mole, respectively), the low solubility of the former contrasts with the high solubility of the latter in petroleum ether and similar solvents. The increased solubility of $(C_5H_5)_2Mn$ in solvents of high dielectric constant, e.g., tetrahydrofuran, glycol dimethyl ether, and pyridine, must be attributed to the solvation energy in such solvents; the concentration of manganous ions in these solvents, as shown by the comparatively small conductivity, is rather small, so that it is more likely that it is the $(C_5H_5)_2Mn$ ion-triplet that becomes solvated rather than the manganous ion. The tendency to solvate is shown by the formation of the ammonia and tetrahydrofuran solvates.

The $C_5H_5^-$ ion is isoelectronic with benzene and the tropylium cation,[10] and is stabilized by delocalization of its π-electrons, although the molecular orbitals occupied will not be precisely the same as in benzene. This, together with the negative charge, results in the anion having chemical properties which are ethylenic in nature as opposed to aromatic, and the behaviour of C_5H_5Na, $(C_5H_5)_2Mg$, $(C_5H_5)_2Mn$, and the rare-earth cyclopentadienides, may be expected, as is found to be the case, to be quite different from that of ferrocene.

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Substituted cyclopentadienes might be expected to form manganese derivatives which are ionic in nature like $(C_5H_5)_2Mn$. The iron, manganese, and some rare-earth compounds have been prepared from sodium methylcyclopentadienide.[25] Manganese methylcyclopentadienide behaves chemically like manganese cyclopentadienide, whilst 1,1-dimethylferrocene closely resembles ferrocene; both are crystalline solids melting a little above room temperature.

In contrast to the behaviour of manganese, rhenium does not form a divalent compound, but gives the compound $(C_5H_5)_2ReH$ where the metal-to-ring bonds are of the ferrocene type.[32]

Since we have compared $(C_5H_5)_2Mn$ with other metal compounds in assessing its ionic properties, it is pertinent to discuss here the bearing of the chemical evidence on the nature of the metal-to-ring bonds in other $(C_5H_5)_2M$ compounds, particularly those of V and Cr.

The evidence clearly indicates that any heteropolar contribution to the bonding in $(C_5H_5)_2Fe$, $(C_5H_5)_2Co$, and $(C_5H_5)_2Ni$ is negligible, and the compounds are unequivocally "sandwich bonded" in all physical states. The fact that only ferrocene fails to react with maleic anhydride and behaves as an aromatic system[19, 26] does not necessarily indicate that the C_5H_5 rings in the Co and Ni (or indeed of the V and Cr compounds also) are of a nature appreciably different from the C_5H_5 rings in ferrocene, since in addition to reactions such as uncatalysed Friedel-Crafts reactions, the *paramagnetic nature of all the molecules other than ferrocene and their ease of oxidation will have a considerable effect on their chemical reactivity*. At the other extreme, manganese, and scandium[14] at the beginning of the first transitional series, give ionically bonded compounds. There is no reason, however, why compounds with metal-ring bonds of an intermediate nature cannot exist, and the chemical behaviour of $(C_5H_5)_2V$ and $(C_5H_5)_2Cr$ strongly suggests that this is indeed so.

The mass spectrographic data[17] and the solubilities of $(C_5H_5)_2V$ and $(C_5H_5)_2Cr$ in non-ionizing solvents clearly indicates that the free molecules are of the ferrocene type with metal-to-ring bonds of primarily "sandwich" type. Also, their inertness

[32] G. WILKINSON and J. M. BIRMINGHAM, *J. Amer. Chem. Soc.*, 77, 3421 (1955).

to water indicates that they are primarily homopolar in the crystal phase. Under certain conditions, however, ionic behaviour is manifested.

The formation of ammoniates and the conductance of liquid ammonia solutions of $(C_5H_5)_2V$ and $(C_5H_5)_2Cr$ shows that in a solvent of high dielectric constant which cannot, like water, cause hydrolysis, ionic dissociation can occur.

The chromium compound differs from $(C_5H_5)_2V$ in that the predominating reaction with hydrogen ion is the formation of cyclopentadiene, and, with ferrous chloride, of ferrocene; only traces of these products are formed with $(C_5H_5)_2V$. For both $(C_5H_5)_2V$ and $(C_5H_5)_2Cr$ with hydrogen ion or ferrous chloride there can thus in principle be two competing reactions: (a) simple oxidation of the metal to a higher and more stable oxidation state where the product has the "sandwich bonded" structure unchanged; (b) ionic metathesis, possibly followed by oxidation, in which both rings need not necessarily be lost. For $(C_5H_5)_2V$, reaction (a) must proceed at a rate greatly in excess of that of reaction (b), whilst for $(C_5H_5)_2Cr$, the reaction (b) is favoured. It should be noted that the course of the reactions may well depend on the conditions and on the temperature.

The following points seem to be relevant to the behaviour of $(C_5H_5)_2V$ and $(C_5H_5)_2Cr$. The magnetic properties of these compounds, which have respectively three and two unpaired electrons, are in accord with the molecular orbital treatments of the "sandwich bond" by MOFFITT and by DUNITZ and ORGEL. In the case of vanadium, the lower *s-d* hydrid orbital (ha_g), which according to MOFFITT results from the mixing and splitting of *s*- and *d*-orbitals under the influence of the π-electron field of the C_5H_5 rings, must be only slightly below those of the other *d*-orbitals (e_{2g}) in the molecule, so that Hund stabilization can occur. The chromium necessarily has two unpaired electrons on MOFFITT's scheme. It is to be noted, however, that ionic forms can be written for these molecules which have the same number of unpaired electrons as the "sandwich bonded" molecules, and consequently resonance between ionic and covalent forms is permissible. In the chromium compound, the *s-d* splitting would also occur even if, in the extreme, one ring were ionically bonded and the other "sandwich bonded."

Whilst the chromium atom is somewhat smaller and the first ionization potential higher than vanadium, $(C_5H_5)_2Cr$ nevertheless appears to have a greater tendency to ionic behaviour, as indicated by the simultaneous reactions of oxidation and hydrolysis or metathesis with $(C_5H_5)_2Cr$, as contrasted to predominantly oxidation with vanadium. It seems unlikely from other evidence that in the free molecules there is any appreciable difference in the metal-to-ring bonding. The difference may be merely a matter of oxidation potential of the metal atom in the compound. A high positive oxidation potential would favour an oxidation rather than a hydrolytic mechanism and, depending on the rates, the former might even proceed exclusively. The smaller size of the chromium also suggests that the energy of solvation could be greater in this case, which would favour greater ionic reactivity independent of the actual nature of the metal-ring bond.

In both $(C_5H_5)_2V$ and $(C_5H_5)_2Cr$, as contrasted with the iron, cobalt, and nickel compounds, there are incompletely filled *d*-orbitals. Since in the molecules a considerable portion of the metal atom between the rings is exposed, the approach of solvent molecules with a high dielectric constant, and the field resulting from them, may affect the energy levels in the metal atom in the compound and alter the nature

of the metal-ring bonding. That such an effect occurs is shown by the solvation and conductance in solution in polar solvents of $(C_5H_5)_2V$ and $(C_5H_5)_2Cr$. Solvation effects occur with other "sandwich bonded" compounds. Thus, although the $[(C_5H_5)_2Co]^+$ ion behaves chemically like the heavier alkali metal ions, unlike the halides of cesium or rubidium, the cobalticinium halides are exceedingly deliquescent; the dependence of the ultra-violet spectrum of ferrocene on the nature of the solvent[33] may also be due to solvation effects.

4. EXPERIMENTAL

Materials and Techniques

Reagent grade chemicals were used. Anhydrous manganous bromide was made by dissolving manganous carbonate (made by precipitation of manganous nitrate solution with sodium bicarbonate) in 48 per cent hydrobromic acid; the solution was evaporated to dryness on a hot plate and, after being finely ground, the product was heated at 200°C in vacuum for two to three hours.

Commercial tetrahydrofuran and ethyleneglycol dimethyl ether were freed from water, alcohol, and peroxides by passing them through columns of Linde Air Products Co. "Molecular Sieves" (Type 13A $\frac{1}{16}$-in. pellets). For special purposes such as conductivity measurements, tetrahydrofuran was distilled over lithium aluminium hydride in a vacuum system.

The $(C_5H_5)_2M$ compounds of Mn and Mg were handled either in vacuum or in a purified nitrogen or argon atmosphere. A gloved box which could be pumped out to 0·1-micron pressure and filled with inert gas was used for many operations.

Analyses

The compounds were destroyed for metal analyses by treatment first with water and then with sulphuric acid to fuming. Magnesium was determined by the phosphate method[34] and in small quantities by colorimetric methods;[35] manganese was determined by weighing the sulphate and by the periodate oxidation method.[34]

Carbon and hydrogen analyses were performed for us by the Linde Air Products Co., Tonawanda, N.Y.[36]

Manganese(II) cyclopentadienide

The preparation was carried out in a nitrogen atmosphere. To sodium shot (10 g) in tetrahydrofuran (150 ml)[37] was added slowly cyclopentadiene (37 ml); hydrogen is rapidly evolved and a solution of C_5H_5Na formed. The colour of the solution varies somewhat with the purity of the solvent and on completeness of removal of air. Clear pale-orange or red solutions are obtained with good conditions, but dark red or purple solutions may be obtained in the presence of traces of air without, however, any serious lowering of the yield. To the cold reagent, finely divided manganous bromide (40 g) was added and the mixture refluxed for two to three hours.[38] The solvent was removed in vacuum, and the product transferred to a sublimation apparatus; at 100–130°C at 10^{-4}-10^{-5} mm Hg, $(C_5H_5)_2Mn$ sublimed in amber crystals, dark brown in the mass,

[33] L. KAPLAN, W. L. KESTER, and J. J. KATZ, *J. Amer. Chem. Soc.*, **74**, 5531 (1952).
[34] *Scott's Standard Methods of Analysis*, N. H. FURMAN, Editor, 5th edition, Vol. I, D. Van Nostrand, New York (1939), p. 532.
[35] E. B. SANDELL, "Colorimetric Determination of Traces of Metals," *Interscience*, New York (1944), pp. 305, 312.
[36] We are indebted to Dr. E. O. BRIMM for his most welcome help in this matter.
[37] Sodium cyclopentadienide is less soluble in glycol dimethyl ether than in tetrahydrofuran, and precipitates as white crystals; the yields are not affected. It may be noted that the use of these solvents and also of dimethylether, which is also effective, as solvents for the reactions of hydrocarbons with sodium is quite old (N. D. SCOTT, J. F. WALKER, and V. L. HANSLEY, *J. Amer. Chem. Soc.*, **58**, 2442 (1936)) although they do not appear to have been used in the present reaction by others.
[38] If the halide is not thoroughly anhydrous, little reaction may occur at this point, but lower yields (~20 per cent) of $(C_5H_5)_2Mn$ may be obtained in a solid-phase reaction by ignition of the dried reaction mixture at 200–250°C.

in yields of the order of 45 per cent based on the bromide. Manganous chloride and iodide reacted similarly.[39]

The compound forms lozenge-shaped biaxial crystals which are highly birefringant. It reacts at once with air or oxygen in the solid state or in solution; when finely divided it will inflame explosively in air. With water or alkaline solutions it effervesces briskly, giving cyclopentadiene and the hydroxide, and with acids the salt and cyclopentadiene. The compound is sparingly soluble in CS_2, CCl_4, and $CHCl_3$, and appears to react with them. It is moderately soluble in benzene (10–15 mg/ml), diethylether (~20 mg/ml), cyclohexane (~5 mg/ml); it is more soluble in pyridine, and particularly so in tetrahydrofuran. It is almost insoluble in petroleum ether. There is only a very slow reaction with carbon dioxide either in the solid state or in solution; this is in contrast to the behaviour of $(C_5H_5)_2Mg$, and must be attributed to the difficulty of carbon dioxide addition to the manganese ion. In benzene solution it reacts instantaneously with benzene solutions of maleic anhydride, giving an orange gelatinous precipitate which has not been characterized but is similar to those given by C_5H_5Na and $(C_5H_5)_2Mg$.

On heating $(C_5H_5)_2Mn$ in an evacuated sealed tube, a sharp colour change occurs at 159–160°C, the amber crystals becoming a very pale pink (almost white for thin specimens). This change is completely reversible. The pink form melts sharply at 172–173°C to a red-brown liquid which may be heated for several hours at temperatures up to 320° with only slight decomposition, a metal mirror forming on the glass walls. The vapour is also thermally stable to at least 350°. Magnetic measurements have shown that the pink form can be quenched by rapid cooling in a dry ice–acetone bath, but not as originally thought,[1] completely; quenched samples have magnetic susceptibilities at 25°C varying irreproducibly, but all appreciably higher than that of the pure brown form at 25°C. Single crystals of the pink form can be grown directly by allowing the vapour to condense on surfaces held between 160°C and 172°C.

Microscopic examination of the brown and pink forms of $(C_5H_5)_2Mn$ suggests that the former is rhombic and the latter monoclinic, but certain designation must await X-ray analysis.*

Vapour Pressure of Manganese Cyclopentadienide

The vapour pressure of $(C_5H_5)_2Mn$ was measured over the range 298° to 525°K, using a quartz spiral gauge as a null instrument. Pressure values could be determined with a maximum error of 1 per cent, and the temperature of the sample and gauge was controlled to ±0·1°C. From the measurements we obtain the following data:

For the solid: $\log P_{mm} = 10{\cdot}58 - 3780/T$, heat of sublimation 17·3 kcal/mole, heat of fusion 6·3 kcal/mole.

For the liquid: $\log P_{mm} = -5{\cdot}93 - 2615/T$, heat of vaporization 12·0 kcal/mole, normal boiling-point 245°C, Trouton's constant 23·1.

These values should be compared with those for ferrocene.[33] It should be noted that no change in the slope of the vapor pressure curve of solid $(C_5H_5)_2Mn$ could be detected between the transition point at 432°K and the melting point. It must be assumed that the brown and pink forms of the solid have similar thermodynamic properties.

Solvation of Manganese Cyclopentadienide

On evaporation of the yellow solutions of $(C_5H_5)_2Mn$ in tetrahydrofuran, a white crystalline product remains. The vapour pressure of ether over this material is of the order of several centimetres of mercury, and the ether is readily removed either by pumping or merely by cooling part of the vacuum system in a dry-ice bath; the brown $(C_5H_5)_2Mn$ then remains. The formation and dissociation of the etherate are completely reversible. Analysis of samples of the white material at −10°C in equilibrium with tetrahydrofuran at 25°C gave the $(C_5H_5)_2Mn$ to C_4H_8O ratio of approximately 2. The glycol dimethyl etherate is more stable, and sublimes in vacuum.

Evaporation of liquid-ammonia solutions of $(C_5H_5)_2Mn$ leaves a white crystalline residue with an ammonia dissociation pressure at 25°C of about 50 cm. An ammoniate of the formula $(C_5H_5)_2Mn \cdot 6NH_3$ has been reported by FISCHER and JIRA,[9] although no analyses were given. At

* See *note added in proof*, p. 104.

[39] We have recently found that manganous bromide prepared from powdered manganese metal by the action of bromine in glycol dimethyl ether gives better yields of the order of 75 per cent.

high ammonia pressures, the ammonia adduct can be sublimed without appreciable decomposition. On pumping on the white ammoniate in a vacuum system, ammonia cannot be completely removed at 25°C, and analysis indicates approximately four ammonia molecules per molecule $(C_5H_5)_2Mn$; on warming, ammonia is completely removed, leaving the brown $(C_5H_5)_2Mn$. Addition of smaller mole ratios of ammonia to $(C_5H_5)_2Mn$ has led to pale pink to white materials of variable composition.

Magnesium Cyclopentadienide

An ether solution of magnesium cyclopentadienide bromide was prepared by addition of cyclopentadiene to an ethylmagnesium bromide reagent,[18] and the solvent removed in vacuum. The dry product was transferred to a sublimation apparatus; on heating at 200–230°C at 10^{-4} mm Hg, the product sublimes as colourless crystals in about 40 per cent yield.

Magnesium cyclopentadienide is decomposed by air or oxygen, although it seems less sensitive to these agents than is $(C_5H_5)_2Mn$. It reacts violently with water, effervescing to give cyclopentadiene and magnesium hydroxide. In the solid state it ignites in carbon dioxide, but in ether solutions can be carbonated like potassium cyclopentadienide;[19] the latter method has in fact been used[2, 4] as a method of separating other $(C_5H_5)_2M$ compounds from magnesium cyclopentadienide when the Grignard reagent is used in their preparation. The compound reacts similarly with carbon disulphide, but it is soluble in ether, benzene, and similar solvents, without decomposition. The molten compound is stable to at least 300°C. With maleic anhydride in ether or benzene solution an orange-red precipitate resembling that obtained with $(C_5H_5)_2Mn$ is formed at once.

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Bis-cyclopentadienylcobalt(II), chromium(II), vanadium(II)

The reaction of the metal halides with sodium cyclopentadienide in glycoldimethylether solution is a much simpler preparative method than those previously described for these compounds. Sodium cyclopentadienide (1 mole) was reacted with either cobaltous chloride (0·5 mole) prepared by dehydration of the ordinary salt at 200°C in vacuum, chromium trichloride (0·25 mole) prepared by the action of carbon tetrachloride on the hydrated salt at 400°C, or vanadium trichloride (0·25 mole) prepared by heating vanadium tetrachloride which in turn was prepared by chlorination of the metal at 500°C. The halides were added to the cooled reagent as solids. After being stirred for two hours the solvent was removed in vacuum, and the *bis*-cyclopentadienyl compounds sublimed directly from the mixture at 150–200°C at 10^{-4} mm Hg. The yields were of the order of 75–80 per cent, based on the halides.

Ferrocene by the Sodium Cyclopentadienide Method

Ferrous chloride in a reactive form is prepared by the reduction of anhydrous ferric chloride (27·1 g, 0·166 mol) with a small excess of iron powder (5·2 g, 0·092 mol) in either tetrahydrofuran or glycoldimethylether solution (150 ml). The mixture is heated until the yellow colour of ferric chloride disappears (~2 hours); a nitrogen atmosphere is maintained over the mixture during this time. A solution of sodium cyclopentadienide (0·5 mol) in 200 ml solvent is slowly added to the ferrous chloride and the mixture stirred with moderate heating for one to two hours. The solution is then filtered or centrifuged and the ferrocene recovered by evaporation of the solvent and crystallization from petroleum ether or by sublimation. Yield 40–42 g (85–90 per cent).

Although quantitative yields of ferrocene have been obtained from the reaction of ferrous chloride with $(C_5H_5)_2Mg$ and $(C_5H_5)_2Mn$ (see below), the lower yields in the above preparation may be due to reduction of cyclopentadiene to cyclopentene during the reaction of the former with sodium. In the reaction of liquid-ammonia solutions of sodium with cyclopentadiene, about 30 per cent of the diene is reduced,[24] but in the ether medium reduction obviously does not occur to this extent.

Ferrocene by the Amine Method

Using the ferrous chloride prepared as above, the yields of ferrocene, utilizing the amine method of preparation,[40] can be very substantially increased. The low yields found previously must be attributed primarily to the low reactivity of the ferrous chloride which had been prepared by high-temperature reduction and secondarily to the use of a solvent as reaction medium.

[40] J. M. Birmingham, D. Seyferth and G. Wilkinson. *J. Amer. Chem. Soc.*, **76**, 4179 (1954).

Ferrous chloride (0·25 mol) is prepared as above. The ether solvent is then almost completely removed under reduced pressure. A mixture of cyclopentadiene (0·5 mol, 42 ml) and diethylamine (~1 mol, ~100 ml) is added slowly, with cooling. The mixture is stirred rapidly at room temperatures for six to eight hours, and the excess of amine then removed under reduced pressure. The residue is extracted with petroleum ether, the extract filtered, and the solvent stripped off. Yield of ferrocene 39–41 g (84–88 per cent of theory). $(C_5H_5)_2Co$ and $(C_5H_5)_2Ni$ can be prepared in similar yields from the dibromides.

Magnetic Measurements

All measurements were made by the Gouy method. The data of Tables 2–4 are representative results from this laboratory; measurements on solid $(C_5H_5)_2Mn$ over the entire range of temperature and on solutions were made in other laboratories.[41] In all, samples from seven different preparations of $(C_5H_5)_2Mn$ were measured on four different balances, and all data agreed within experimental error (~3 per cent). For all measurements the tube was suspended in a nitrogen atmosphere.

TABLE 2.—MAGNETIC SUSCEPTIBILITY OF $(C_5H_5)_2Mn$; REPRESENTATIVE DATA

Temperature °K	$\chi_{mol}^{corr} \times 10^{6}$* at various field strengths, in Gauss				$2{\cdot}83\sqrt{\chi_{mol}^{corr}\,T}$	
	6050	4950	3750	2600	at $H = 4950$	Average over all fields
77 ± 1	10,100	10,000	10,000	9,910	2·49	
113 ± 1	10,900	10,850	10,780	10,700	3·14	
144 ± 1	11,080	11,030	11,060	10,960	3·57	
154 ± 1	11,000	10,990	10,970	10,930	3·68	
196 ± 1	10,730	10,710	10,600	10,530	4·10	
262 ± 1	9,990	9,970	9,910	9,820	4·57	
292 ± 0·5	9,480	9,400	9,380	9,330	4·68	
296 ± 0·5	9,500	9,430	9,400	9,230	4·73	
351 ± 1	8,900	8,800	8,600	8,500	4·98	
418 ± 2	8,040	7,920	7,880	7,850	5·14	
438 ± 4	10,300	10,200	10,400	10,100		5·95
467 ± 4	9,170	9,200	9,150	9,180		5·86
496 ± 4	8,600	8,690	8,710	8,570		5·86

* χ_{mol}^{corr} includes a diamagnetic correction of -90×10^{-6} cgsu for the C_5H_5 rings.

Low temperatures were obtained using cooling baths of liquid nitrogen, dry-ice–acetone, ice-salt, and slush baths of various organic liquids. High temperatures were obtained using a non-inductively wound furnace. Pyrex tubes with a dividing septum were used, the bottom section being evacuated. The measurements were repeated over periods of twenty to thirty minutes to ensure thermal equilibrium. Two thermocouples were used, one at the septum and the other at the top of the sample. For low-temperature measurements the thermal gradient was zero over the length of the sample (~12 cm), and the small error in Tables 2 and 3 is inherent in the measurement of the e.m.f. of the thermocouple. The furnace was constructed to keep the upper part of the sample tube slightly warmer than the lower part in order to prevent sublimation of the $(C_5H_5)_2Mn$ to the top of the tube. The error in temperature listed for these measurements is based on this thermal gradient.

[41] We are indebted to Dr. NORMAN ELLIOT of the Brookhaven National Laboratory and Prof. K. A. JENSEN of the University of Copenhagen for so kindly allowing us to use their balances for series of measurements, and to Prof. R. W. ASMUSSEN and Mr. SOLING of Chemistry Dept. B, Technical University of Denmark, for carrying out several measurements for us, during the spring of 1954.

TABLE 3.—MAGNETIC SUSCEPTIBILITY OF $(C_5H_5)_2Mn$-$(C_5H_5)_2Mg$. MIXTURE—8·06 MOLE PER CENT Mn

Temperature °K	$\chi_{gm} \times 10^6$ for mixture*	χ_{mol}^{corr}† $\times 10^3$ for $(C_5H_5)_2Mn$	$2{\cdot}83\sqrt{\chi_{mol}^{corr} T}$
77 ± 1	26·5	5·32	5·73
151 ± 1	14·3	2·94	5·97
196 ± 1	10·6	2·21	5·89
262 ± 1	8·03	1·71	5·98
292 ± 0·5	7·08	1·52	5·97
325 ± 1	6·43	1·40	6·03
375 ± 1	5·3	1·17	5·92
400 ± 2	4·6	1·04	5·77
416 ± 2	4·6	1·04	5·87
426 ± 3	4·5	1·02	5·90
438 ± 4	4·5	1·02	5·98
			Av. = 5·94 ± 0·05

* Measurements were made only at fields of 6050 and 4950 gauss. No dependence on field strength was observed.

† χ_{mol}^{corr} includes diamagnetic correction for C_5H_5 rings.

TABLE 4.—MAGNETIC SUSCEPTIBILITY OF $(C_5H_5)_2Mn$ IN SOLUTIONS AT 21°C

Solvent	Conc mg/ml	χ_{mol}^{corr}* $\times 10^6$	$2{\cdot}83\sqrt{\chi_{mol}^{corr} T}$
Ether	10·0	13,520	5·72
Ether	11·8	14,300	5·87
Benzene	10·0	13,800	5·74
Benzene	17·3	15,400	5·92
			Av. = 5·81 ± 0·10

* χ_{mol}^{corr} includes diamagnetic correction for C_5H_5 rings.

Calibrations were made with MOHR's salt, using the susceptibility data of JACKSON.[42]

Samples of $(C_5H_5)_2Mn$ and $(C_5H_5)_2Mg$ were sublimed through porous plugs into Pyrex tubes which were sealed off; these were broken in an argon atmosphere in the gloved box, and the compounds transferred to a vessel provided with a heavy glass ball for grinding the material, and with a ground joint and stopcock. For evacuation the Gouy tube was sealed to the upper part of the vessel, and, after transfer to it of the material ground in vacuum, it was sealed off. Solid solutions of $(C_5H_5)_2Mn$ in $(C_5H_5)_2Mg$ were prepared by subliming a mixture of the compounds in approximately the desired proportions into a large glass tube, which was then sealed off. The material was then melted and agitated. The solidified melt was handled like the pure compounds. The manganese content was determined by analysis of a sample of the solution. The magnetic susceptibility of $(C_5H_5)_2Mg$ was measured at 298°K and 90°K; χ_{mol} was $-108 \pm 4 \times 10^{-6}$ c.g.s.u., independent of field and temperature.

The value of the susceptibility of the high-temperature form of $(C_5H_5)_2Mn$ given previously[1] was incorrect, due to use of an impure sample and faulty technique, and must be discarded. The

[42] L. C. JACKSON, *Phil. Trans. Roy. Soc.* (London), **A224**, 1 (1923).

values of the susceptibilities of $(C_5H_5)_2Mn$ at 291°, 435°, and 445°K, given by FISCHER,[3] appear to be in serious error; only the value at 90°K is in agreement with the results in this paper. No field-strength dependence was noted, nor are the fields used in the measurements specified. The values deviate so far from the present data, which are representative of several determinations under widely different conditions of sample preparation and measurement, that they must be considered meaningless. The measurement by ENGELMANN[43] of the "white $(C_5H_5)_2Mn$" prepared by FISCHER is also of little value, since it was subsequently discovered[44] that the sample contained nitrogen, and was presumably an ammoniate of indefinite composition.*

Exchange Measurements

A dilute hydrochloric acid solution of ~0·2 mc Fe^{59} radioactive tracer (Isotopes Division, U.S.A.E.C., Oak Ridge, Tenn.) was reduced with sulphur dioxide and evaporated to a few drops. Five ml of a 1-mg/ml solution of ferrocene in thoroughly deoxygenated ethanol was added, and the solution allowed to stand in an evacuated vessel at 25°C. Ferrocene was recovered from an aliquot by evaporation and sublimation in vacuum; it was destroyed by nitric acid, and this solution evaporated and ignited on a platinum disc for counting in a flow proportional counter. No activity above natural background has been detected over a period of twelve months, and it seems safe to conclude that there is no exchange between the iron atom of ferrocene and the ferrous ion.

Infra-red Spectra

In an argon atmosphere in the gloved box, small (0·5–1 mm) crystals of $(C_5H_5)_2Mn$ and $(C_5H_5)_2Mg$ were separately placed between silver chloride windows (1·5 × 2·5 × 0·1 mm); the edges of the windows were then sealed with a low-melting black wax. A crystal of ferrocene was mounted similarly. The measurements were made on a Perkin-Elmer Model 21 Double-beam recording infra-red spectrometer with a microscope attachment in the sodium chloride and calcium fluoride regions.[45]

Chemical Reactions

Samples of the $(C_5H_5)_2Mn$ compounds were sublimed into break-seal tubes, which were then sealed to the vacuum system for admission of gases and of solvents by condensation. Reactions of the compounds with various reagents were carried out, using solutions of the compounds and reagents prepared separately in break-seal tubes. The break-seals were then broken and the reactants mixed.

* *Note added in proof.*

Magnetic susceptibility measurements on $(C_5H_5)_2Mn$ have again been published by E. O. FISCHER [E. O. FISCHER and H. LEIPFINGER, *Z. Naturforschg.*, **10b**, 353 (1955)]. These latest values agree neither with the present work, nor with FISCHER's own previous work.[3] The new results are not given in detail but are shown only graphically. Study of this graph shows that the variation of the susceptibility with temperature between 77°K and 430°K (which is the transition temperature at 158°C, erroneously listed by FISCHER and LEIPFINGER as 158°K) is quite different from that found by us. There is no evidence of the Neél point on FISCHER's plot. In fact, none of the numerical values which can be estimated from the graph for χ at various temperatures are in agreement with our data except at 77°K and above the transition temperature. FISCHER now reports $\chi_{mol}^{291} \simeq \chi_{mol}^{435} \simeq \chi_{mol}^{445} \simeq +8900 \times 10^{-6}$ cgsu; his previous values for the same temperatures were $+6100 \times 10^{-6}$ cgsu. No comment is made on this discrepancy and it is difficult to know which of the values FISCHER himself regards as correct. The field strengths at which the measurements were made were again not specified. The use of different field strengths may, in part, account for the difference between FISCHER's results and ours, and of the discrepancies in his own work. However, much of his data diverges from ours too far to be attributed to this cause, and further, the fundamentally different form of a plot of his χ values *vs.* temperature cannot be accounted for in this way.

It is also surprising that a solution of 53% $(C_5H_5)_2Mn$ in $(C_5H_5)_2Mg$ shows complete absence of co-operative phenomena as is implied by FISCHER's data, where it is shown that the susceptibility of the manganese atoms in such a mixture follows the Curie-Weiss law. Mixed crystals of higher than 10–15 mole % $(C_5H_5)_2Mn$ are yellow-orange, and it is only in mixed crystals of lower manganese content that the pink colour of the Mn^{++} ion is observed; it was for this reason that a dilute mixture was measured in the present work. An explanation may be that the co-operative phenomena in $(C_5H_5)_2Mn$ require not only the closeness of the manganese ions but also the arrangement peculiar to the rhombic crystal lattice of the pure compound. This matter should be examined further.

[43] F. ENGELMANN, *Z. Naturforschg.*, **8b**, 775 (1953).

[44] E. O. FISCHER (private communication).

[45] We are indebted to Dr. E. R. BLOUT of the Polaroid Corporation, Cambridge, Mass., for kindly allowing us to use this instrument.

Ferrous Chloride Reactions

The salt was prepared in a reactive form by refluxing the theoretical amounts of anhydrous ferric chloride and iron powder in glycoldimethylether or tetrahydrofuran solution under nitrogen. This ferrous chloride is appreciably soluble in these solvents. Weighed ampoules of various compounds were broken under the surface of the reagent and the weight of compound computed later by weighing the glass fragments. After the reaction, the solvent was removed in vacuum and the residue extracted with air-free petroleum from which any ferrocene was obtained by evaporation.

$(C_5H_5)_2Mn$, Mg. The reaction is instantaneous and quantitative at 25°C. In a typical reaction 1·0925 g $(C_5H_5)_2Mn$ gave 1·098 g ferrocene.

$(C_5H_5)_2V$. Macroscopic quantities of ferrocene were not formed. A faint blue colour was observed on treating the petroleum extract with 4N HNO_3, indicating the ferricinium ion in quantities probably of the order of a milligram or less from gram amounts of $(C_5H_5)_2V$. An indigo solution of $(C_5H_5)_2VCl$ is formed; this was oxidized by hydrochloric and nitric acids to $(C_5H_5)_2VCl_2$, and in water gave the usual *bis*-cyclopentadienyl cation reactions such as precipitation with silicotungstic acid.

$(C_5H_5)_2Cr$. In a typical experiment, 1·036 g $(C_5H_5)_2Cr$ gave 0·752 g ferrocene after refluxing for one hour, although the reaction is instantaneous at 25°C. The nature of the green product formed simultaneously is being investigated. If $FeCl_2$ prepared from hydrated ferric chloride, $FeCl_3 \cdot 6H_2O$, in glycoldimethylether, is used, yields of ferrocene of the order of 40 per cent are obtained.

$(C_5H_5)_2Co$. Ferrous chloride is reduced to metallic iron and cobalticinium chloride formed quantitatively.

$(C_5H_5)_2Ni$. No reaction to give ferrocene after seventeen hours under reflux. The $(C_5H_5)_2Ne$ was destroyed by air oxidation before attempts to isolate ferrocene were made.

Conductivity Measurements

A tube cell with platinized platinum electrodes near the bottom was fitted with a side arm, into which the compounds to be studied could be sublimed and in which solutions were made, and with a stopcock and ground joint for attachment to a vacuum system. The content of the cell tube at reference points was determined and the amount of solute determined after the measurements. The cell constant was determined, using aqueous potassium chloride solutions. Measurements were made with an A. H. Thomas, Philadelphia, "Serfass Conductivity Bridge" Model RCM15.

The solution of C_5H_5Na was prepared *in situ* by adding cyclopentadiene to a solution of sodium in liquid ammonia.

Although the measured conductances of C_5H_5Na, $(C_5H_5)_2Mg$, and $(C_5H_5)_2Mn$ seem to be rather low, the conductances are of the order of 0·25 of the value of comparable concentrations of ammonium acetate in water.

Conducting solutions of somewhat lower specific conductance are also given in tetrahydrofuran solution by C_5H_5Na, and the $(C_5H_5)_2M$ compounds of Mn, Mg, Cr, and V.

Acknowledgements—We are indebted to the General Electric Company for the Swope and Coffin Fellowships (F. A. C.), to the National Science Foundation for a pre-doctoral Fellowship (J. M. B.), and to the Mallinckrodt Chemical Company for assistance with some research expenses. Thanks are due to the John Simon Guggenheim Memorial Foundation for a Fellowship (G. W.) and to Prof. JANNIK BJERRUM, Chemistry Department A, Technical University of Denmark, for the kind hospitality of his laboratories for two of us during the spring of 1954.

This work was also supported in part by the Atomic Energy Commission.

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J. Inorganic and Nuclear Chemistry, 1956, Vol. 2, pp. 114–117. Pergamon Press Ltd., London

THE SEPARATION OF PROTACTINIUM AND ZIRCONIUM BY AN ANION EXCHANGE COLUMN

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(*Received* 18 *August* 1955)

Abstract—Conditions for the separation of zirconium and protactinium by anionic exchange on an Amberlite IRA-400 resin column are described. The separation has been tested at macroscopic concentrations of the elements.

ONE of the difficulties encountered in the purification of protactinium is its separation from zirconium. Solvent extraction from chloride solution offers one possibility, and has been described elsewhere.[1] Anion exchange has been used successfully by other investigators. Both methods depend on the formation of chloro-complexes by the two metals. These probably differ in valence and dissociation constants. In this paper the suitability of different exchange resins for the separation is examined.

KRAUS and MOORE[2] determined the distribution coefficient of protactinium between the strongly basic resin Dowex-1 and hydrochloric acid of different concentrations. They found that protactinium, in tracer concentrations as ^{233}Pa, was practically quantitatively adsorbed from hydrochloric acid at or above 8 M, but that it could be eluted again by a weaker acid, not exceeding 4 M. In a further series of papers[3, 4, 5] the same authors showed that zirconium was only feebly adsorbed from a wide range of hydrochloric-hydrofluoric acid mixtures, and could be separated easily from niobium and tantalum, which were strongly adsorbed, but less easily from protactinium. Hydrofluoric acid markedly diminished the adsorption of protactinium from the chloride solutions, although it is known to give a strong anionic complex with protactinium. HUFFMAN, IDDINGS, and LILLY[6] have made measurements of the distribution of zirconium between Dowex-2 and hydrochloric acid at concentrations between 7 and 11 M. An examination of their data together with those of KRAUS and MOORE[2] shows that while both metals are strongly adsorbed from concentrated (>9 M) hydrochloric acid and only weakly from dilute acids (<3 M), there should be a range of concentrations over which an effective separation might be expected. CRANE, in a compilation of separation procedures,[7] recommends adsorption of the protactinium from 8 M hydrochloric acid on a Dowex-1 column of specified dimensions. The zirconium is washed through with the same concentration of acid and the protactinium finally eluted with 4 M acid. Suitable elution rates are given. In addition to these studies, YANG JENG-TSONG[8] has reported on the separation of

[1] GOLDEN, J., and MADDOCK, A. G. (1956) *J. Inorg. Nucl. Chem.*, **2**, 46.
[2] KRAUS, K. A., and MOORE, G. E. (1950), *J. Amer. Chem. Soc.*, **72**, 4293.
[3] KRAUS, K. A., and MOORE, G. E. (1951), *J. Amer. Chem. Soc.*, **73**, 9.
[4] KRAUS, K. A., and MOORE, G. E. (1951), *J. Amer. Chem. Soc.*, **73**, 13.
[5] KRAUS, K. A., and MOORE, G. E. (1951), *J. Amer. Chem. Soc.*, **73**, 2900.
[6] HUFFMAN, E. H., IDDINGS, G. M., and LILLY, R. C. (1951), *J. Amer. Chem. Soc.*, **73**, 4474.
[7] CRANE, W., and MEINKE, W. W., United States Atomic Energy Commission Declassified Document 2750, December, 1949.
[8] YANG JENG-TSONG. *Compt. Rend.* (1950), **231**, 1059.

tracer concentrations of protactinium and tantalum by anionic exchange of the complex citrates on an Amberlite IR–4B column. Recently KRAUS and MOORE[9] have described the separation of iron and protactinium by anionic exchange.

EXPERIMENTAL

Materials.—Tracer solutions of ^{233}Pa (β^--emitter, $t_{\frac{1}{2}} = 27{\cdot}4$ *d*), ^{231}Pa (α-emitter, $t_{\frac{1}{2}} = 34{,}000$ *y*), and ^{95}Zr (β^--emitter, $t_{\frac{1}{2}} = 65$ *d*) in hydrochloric-hydrofluoric acid mixtures were available. The separation of the protactinium isotopes has already been described.[1] The zirconium was of fission-product origin and no carrier had been added. The fluoride was eliminated by repeated evaporation of the stock solutions with concentrated hydrochloric acid.[1] Equal aliquots were then added to equal volumes of different concentrations of hydrochloric acid. The added aliquots were small enough for the concentration of the acid not to be appreciably changed by their addition. Amberlite IRA-400 and Dowex-2, both strongly basic quarternary amine resins, were ground to pass a 200-mesh sieve. The part retained by a 250-mesh sieve was used. Both resins were converted to the chloride form by previous treatment with pure hydrochloric acid of the concentration to be employed subsequently.

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Distribution Experiments.—The tracer solution (0·5 ml) was agitated with the resin (20 mg) in a polythene ampoule with a push-fit cap. Losses of activity occurred when glass vessels were used. The tubes were equilibrated with mechanical agitation in a thermostat at 20°C for two to six days. In most cases equilibrium was established in less than two days (contrast ref. 2). The ampoules were then centrifuged and the liquid and resin phases separated and assayed for β^- activity and compared with the activity of the original stock solution. Aliquots of the liquid phase were evaporated on platinum discs and the discs gently ignited before counting under a bell-jar counter. It is known that protactinium is not lost during this treatment.[1] The resin phase was separated and dried between filter papers and finally in an oven at 50°C. Weighed amounts (~1 mg) were then spread on platinum discs for counting. In the case of the Amberlite samples, which spread evenly on the discs, there was no difference between the count on discs prepared in this way, or after evaporation with concentrated nitric acid followed by ignition. The latter treatment was found preferable with the Dowex-2 samples. Reproducibility was not as good as is usual in this kind of measurement, but the activity balance was maintained at ± 2 per cent and the duplication reproducibility in a number of experiments was ± 5 per cent. The results are shown in Fig. 1. The distribution coefficient

$$K_d = \frac{\text{activity of 1 g resin}}{\text{activity of 1 ml solution.}}$$

Column Experiments.—To facilitate independent measurement of the protactinium and zirconium by their activities and to allow macroscopic concentrations of the former element to be used, these experiments were conducted with ^{231}Pa- and ^{95}Zr-containing carriers. Between 20 and 100 γ of each element was employed in each experiment. The impossibility of satisfactory recovery of the protactinium when glass apparatus was used was soon established, and the experiments described below were conducted in a polythene column.

The column was filled with Amberlite IRA-400 in the chloride form, sieved 90–100 mesh, the resin bed being 3 mm diameter and 110 mm long. Elutions were conducted at the rate of 2–5 ml/cm^2-min. The column was pre-treated with hydrochloric acid of the concentration to be used first in the subsequent operations. The zirconium-protactinium mixture was added in 2 ml of hydrochloric acid and the column subsequently eluted with pure acid of the same concentration. The effluent liquid was collected in an automatic fraction collector actuated by the number of falling drops. The α and β activities of the fractions were determined after evaporation of aliquots on platinum discs, the α activities being measured with a scintillation counter or a quartz fibre electrometer and ionization chamber.

No significant amount of protactinium was ever found in the effluent when the acid concentration exceeded 6 M. Except at very high acidities (>8 M), nearly all the zirconium was quickly eluted by the acid washing. The protactinium could be eluted in a small volume with dilute hydrochloric acid. The results are shown in Fig. 2.

[9] KRAUS, K. A., and MOORE, G. E. (1955), *J. Amer. Chem. Soc.*, 77, 1383.

DISCUSSION

The three curves for protactinium are similar, though the sharp rise in distribution coefficient occurs at a higher acid concentration with Dowex-2 and Amberlite IRA-400. Both metals are feebly adsorbed below 5 M but strongly adsorbed above 9 M. In

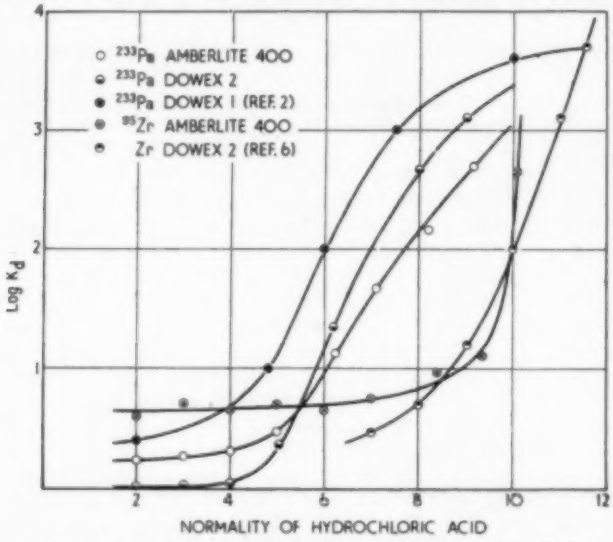
○ ^{233}Pa AMBERLITE 400
◒ ^{233}Pa DOWEX 2
● ^{233}Pa DOWEX 1 (REF. 2)
◉ ^{95}Zr AMBERLITE 400
◓ Zr DOWEX 2 (REF. 6)
Log K_d
NORMALITY OF HYDROCHLORIC ACID

FIG. 1.—Relation between distribution coefficient K_d and molarity of hydrochloric acid for ^{233}Pa and ^{95}Zr on different anion exchange resins.

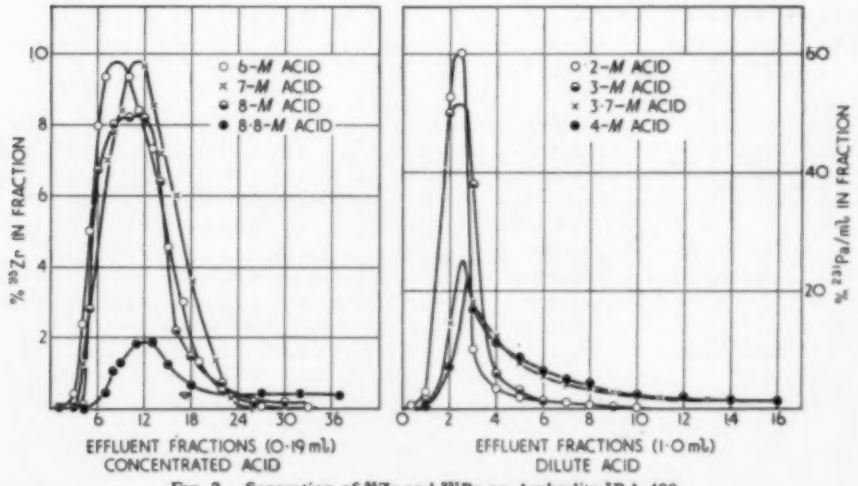

FIG. 2.—Separation of ^{95}Zr and ^{231}Pa on Amberlite IRA-400

6 M hydrochloric acid, the distribution coefficients for Amberlite IRA-400 favour the adsorption of the protactinium by a factor of about 2, while at 8 M the coefficients differ by a factor of about 20. Below 5 M, zirconium becomes more strongly adsorbed by a factor of about 2. Separation might be expected in the acid concentration

range 6–8 M. Above 8 M the ratio of the coefficients is still favourable, but separation would be expected to be slow because both metals are strongly adsorbed.

These conclusions were confirmed by the column experiments, the results of which are shown in Fig. 2. Between 6 and 7 M hydrochloric acid at least 95 per cent of the zirconium can be eluted by 6 column volumes of acid without more than 0.1 per cent of the protactinium. With 8 M acid, separation is still good, but the zirconium is only 85–90 per cent removed by the same volume of acid. At 8·8 M, adsorption of the zirconium is so strong that only 25 per cent is removed when 10 column volumes of acid are passed through the column. The protactinium can be desorbed from the column by washing with dilute hydrochloric acid. To remove the protactinium in a small volume, the concentration of the acid should not exceed 3 M. At this concentration more than 95 per cent of the protactinium can be removed by 10 column volumes of the acid.

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J. Inorganic and Nuclear Chemistry, 1956, Vol. 2, pp. 118–124. Pergamon Press Ltd., London.

HEATS OF SOLUTION OF THE THORIUM NITRATE HYDRATES IN WATER AND IN CERTAIN ORGANIC SOLVENTS*

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(*Received* 8 *July* 1955)

Abstract—Heats of solution of thorium nitrate pentahydrate and tetrahydrate in water and in a number of oxygenated organic solvents have been measured. The relative values of the heats of solution are found approximately to parallel the base strengths of the solvents as established by previously reported heat-of-solution measurements for 2 : 1 salts, and by other established criteria.

THE heats of solution in organic solvents of the hydrates of the 2 : 1 salts uranyl nitrate, cobaltous nitrate, and cobaltous chloride have been previously reported.[1, 2, or 3] Data of this type have been helpful in obtaining information on solute-solvent interactions in nonaqueous solvents and in estimating energies of binding ligand groups to the metal atom.[2] This paper reports on the extension of heat-of-solution measurements to a 4 : 1 salt, thorium nitrate.

EXPERIMENTAL

Materials—Thorium nitrate pentahydrate and tetrahydrate were prepared according to methods already described.[4] The solvents used were in general redistilled at atmospheric pressure from the commercially available products. All ethers were tested for peroxide impurities before use. Acetone was dried over anhydrous potassium carbonate and redistilled. The water content of all solvents was checked by titration with Karl Fischer reagent,[5] and varied from 0·0 to 0·3 per cent.

Analyses—Check analyses were made in duplicate on the hydrates on the day they were to be used. Thorium was determined by ignition to ThO_2, and water was determined by titration with Karl Fischer reagent. The ThO_2 determinations showed a standard deviation of 3 parts in 1000, and the standard deviation of water analyses was 6 parts in 1000 of water. Accuracies of this order of magnitude with a single determination conceivably (but with low probability) could overlook a contamination of 10-mole per cent of one hydrate in the other. This could give an error of 0·4 kcal/mole in the heat of solution, on the basis of the fairly consistent difference between the values for the two hydrates in the same solvent of about 4 kcal/mole.

Apparatus and Procedure—The calorimeter consisted of a cylindrical Dewar flask (685-ml capacity) immersed in a water bath at 25 ± 0·1° to 1 cm from its top. The flask was fitted with a Lucite lid, through which were mounted a glass-enclosed platinum resistance thermometer (ice-point resistance 26 ohms), a breaking device, a heater, a stirrer, and a stirrer well. The heater consisted of 136 ohms of insulated nichrome wire encased in a closely-fitting copper tube, which was wrapped around the bottom 5 cm of the stirrer well. The heater leads, which were of B. and S. No. 30 copper, were brought out of the calorimeter through small Monel tubes that were soldered to

*In part taken from a Ph.D. thesis submitted by JOHN R. FERRARO to the Graduate School of Illinois Institute of Technology, in partial fulfilment of the requirements for the degree of Doctor of Philosophy.
Work performed under the auspices of the U.S. Atomic Energy Commission.
†Chemistry Division, Argonne National Laboratory.
‡Department of Chemistry, Illinois Institute of Technology.
(1) L. I. KATZIN, D. H. SIMON, and J. R. FERRARO, *J. Amer. Chem. Soc.*, **74**, 1191 (1952).
(2) L. I. KATZIN and J. R. FERRARO, *ibid.*, **74**, 6040 (1952).
(3) L. I. KATZIN and J. R. FERRARO, *ibid.*, **75**, 3821 (1953).
(4) J. R. FERRARO, L. I. KATZIN, and G. GIBSON, *J. Amer. Chem. Soc.*, **76**, 909 (1954).
(5) J. MITCHELL, Jr., and D. H. SMITH, *Aquametry*, Interscience Publishers, Inc., New York, N.Y. (1948).

the copper tube containing the heater. The stirrer well was a thin-wall Monel cylinder extending nearly to the bottom of the calorimeter, with openings above the heater to allow for proper circulation of the solution. The stirrer was a cupronickel tube attached to a Monel propeller, and was operated by a synchronous motor. The lower portion of the stirrer well and of the stirrer were gold-plated to prevent reaction with any acid liberated during the course of the measurement.

The following procedure was used in the measurements. A 200-ml volume of the solvent, thermostated at 25°, was added to the calorimeter, the Lucite lid and accessories were put in place, and the openings were sealed with Apiezon "Q." A weighed amount of solute was placed in the breaking device. The solution was stirred, and after equilibration the temperature of the solution was followed with the resistance thermometer for about ten minutes. The sample tube was then broken. After the dissolution of the sample (usually complete within five minutes) the temperature of the solution was again followed with the resistance thermometer until a constant drift was obtained. The solution was then heated electrically for five minutes, with a current of suitable magnitude to produce approximately the same temperature rise (usually about 1°) as the dissolution of the sample, and again the temperature was followed until the drift became constant.

The electrical measurements were made with a calibrated White double potentiometer, a galvanometer with a working sensitivity of 0·04 μV/mm, calibrated resistors, and an unsaturated Weston standard cell. Both the resistance standard and the standard cell were calibrated by the National Bureau of Standards. An electric timer operated by a calibrated tuning-fork and amplifier was automatically started and stopped at the same time as the heater current.

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The apparatus and technique were checked by measuring the heat of solution of anhydrous sodium carbonate. BICHOWSKY and ROSSINI[6] list the heat of solution of one mole of anhydrous sodium carbonate in 200 moles water as 5·88 kcal. Two determinations at this dilution gave 5·91 and 5·80 kcal/mole.

Heats of Solution—The heats of solution of thorium nitrate tetrahydrate and thorium nitrate pentahydrate in water, and in a number of oxygenated organic solvents, are given in Table 1. These are generally the means of two or three determinations.

The original intention was to maintain the salt-solvent mole ratio of 1 : 80 used in earlier investigations. However, in some cases incomplete dissolution of the hydrates or formation of precipitates necessitated larger dilutions. With the tetrahydrate in diethyl malonate, for instance, residues were still encountered at 1 : 730. As a consequence, the solvent-salt mole ratios indicated in Table 1 vary considerably. Questions of heats of dilution must therefore enter into detailed comparisons of the values for the different solvents. However, heats of solution of the two hydrates were obtained for the same dilution in a given solvent.

Possible side reactions must always be kept in mind in systems of organic liquids and nitrate salts. With acetone and methyl ethyl ketone, some yellowing, and poorer checks than normal among duplicate determinations, gave evidence for some side reaction. Another test is possible on comparing the heat of transition between pentahydrate and tetrahydrate from (a) the difference in heats of solution of the two hydrates in water and (b) the difference in heats of solution of the hydrates in the organic solvent, together with the heat effect of adding a mole-equivalent of water to the tetrahydrate solution (Table 3). These differences for ethylene glycol monoethyl ether, ethyl acetate, and ethyl propionate seem to be outside the statistical errors.

The heat of solution of anhydrous thorium nitrate[7] in water was also measured and found to be −34·7 kcal/mole at a dilution of 1 : 2500. The limited solubility of the anhydrous thorium nitrate in the organic solvents prevented the measurements of its heats of solution in these solvents.

DISCUSSION

The relationship between the functional group of the solvent and the order of the heat-of-solution values found for uranyl nitrate, cobaltous nitrate, and cobaltous chloride dihydrates,[1, 2, or 3] is also apparent when one considers the data for thorium nitrate tetrahydrate in Table 1. The ethers and ether-alcohols show high heat evolution, low-molecular-weight ketones show less, and the higher-weight ketones

[6] F. R. BICHOWSKY and F. D. ROSSINI, The Thermochemistry of the Chemical Substances, Reinhold Publishing Corp., New York (1936), p. 144.

[7] J. R. FERRARO, L. I. KATZIN, and G. GIBSON, *J. Amer. Chem. Soc.*, 77, 327 (1955).

TABLE 1.—HEATS OF SOLUTION (ΔH) OF THORIUM NITRATE HYDRATES IN WATER AND IN VARIOUS ORGANIC SOLVENTS AT 25° (KCAL/MOLE)[1]

Solvent/Solute	$Th(NO_3)_4 \cdot 4H_2O$	$Th(NO_3)_4 \cdot 5H_2O$
Tributyl phosphite	−42·9 (480)	−44·2 (80)
		−37·2 (480)[2]
Dimethyl formamide	−25·2 (150)	−21·6 (150)
		−20·0 (293)[2]
Dibutyl butylphosphonate	−18·8 (450)	−14·2 (80)
		−15·5 (450)
Tetrahydrofuran	−14·2 (80)	− 9·4$_0$ (80)
		− 8·9$_7$ (138)[2]
		− 5·9$_5$ (300)[2]
Tributyl phosphate	−12·1 (80)	− 7·6$_5$ (80)
Ethylene glycol diethyl ether	−11·1 (150)	− 6·6$_0$ (150)
Diethyl ether	− 9·5$_5$ (80)	− 4·8$_5$ (80)
		− 4·5$_2$ (110)[2]
		− 3·25 (218)[2]
Ethylene glycol monoethyl ether	− 9·4$_0$ (150)	− 7·0$_5$ (150)
Dibutyl "carbitol"	− 8·4$_0$ (450)	− 3·3$_0$ (450)
Water	− 7·6$_5$ (350)	− 3·5$_5$ (350)
Acetone	− 6·6$_5$ (80)	− 3·3$_5$ (80)
Methyl ethyl ketone	− 5·9$_5$ (130)	− 1·50 (130)
Ethyl acetate	− 1·41 (200)	3·10 (165)
		1·04 (200)[2]
Methyl isobutyl ketone	− 1·19 (300)	1·74 (100)
		0·37 (300)[2]
Ethyl propionate	1·05 (150)	4·4$_5$ (150)
Ethyl chloroacetate	1·38 (300)	4·7$_0$ (300)
n-Amyl acetate	1·10 (200)	4·6$_5$ (130)
		5·0$_7$ (200)[2]
Isobutyl alcohol	1·65 (180)	6·3$_5$ (180)
Diethyl malonate		9·8$_5$ (700)

(1) The numbers in parenthesis indicate the solvent/solute mole ratios.
(2) Single determinations.

and the esters give the lowest heat evolution. Dimethyl formamide, tributyl phosphate, and dibutyl butyl phosphonate act like the ethers and alcohols, as was found in the earlier data. In tributyl phosphite the heats-of-solution values are considerably higher than those shown by the ethers and alcohols. This singularly high value for the heat of solution in tributyl phosphite correlates with the presence of a pair of free electrons on the phosphorus, and leads to the inference that with this compound direct co-ordination of phosphorus to the thorium ion is involved. A corollary is that, in the two other phosphorus compounds (tributyl phosphate and dibutyl butyl phosphonate), the binding is through the oxygens, since the heat effects are similar to those with the other strong-base oxygenated liquids. No conclusion can be drawn from these results alone as to the possible role of the non-ester oxygen of these phosphate derivatives.

The heat of solution in isobutyl alcohol falls anomalously among the weaker-base esters. A similar anomaly was found with the 2 : 1 salts,[1, 2, or 3] and was ascribed to the

endothermic effects of displacement of anions from the cation co-ordination sphere in the pure alcohol. This would mask part of the heat evolved from co-ordination of the alcohol in other positions. Solution in a mixture of the alcohol with another (weak base) solvent such as acetone gave a higher heat evolution than the pure alcohol. This heat evolution was equivalent to that of the other strong electron donors, through eliminating the anion replacement reaction. The results of similar experiments with thorium nitrate solutions are exhibited in Table 2. For both isobutyl alcohol in acetone and water in acetone there is a heat evolution equivalent to that in the other strong bases.

TABLE 2.—HEATS OF SOLUTION OF $Th(NO_3)_4 . 4H_2O$ IN MIXTURES OF ISOBUTYL ALCOHOL OR WATER WITH ACETONE

Solvent	Vol. per cent Mixture with Acetone	ΔH (kcal/mole)
Water	0	$-6{\cdot}6_6$
	40	$-12{\cdot}0$
	50	$-9{\cdot}1_5$
	75	$-7{\cdot}4_8$
	100	$-7{\cdot}6_4$
Isobutyl alcohol	0	$-6{\cdot}6_5$
	50	$-8{\cdot}0_5$
	75	$-11{\cdot}4$
	87·5	$-7{\cdot}9_0$
	100	1·65

A more direct comparison of electron-donor strengths of solvents than the heat-of-solution comparison is obtained by comparing base strengths against a standard (water).[1–3] This is accomplished by measuring the change in heat effect of adding one mole equivalent of water to a solution of thorium nitrate tetrahydrate in an organic solvent, compared to addition to pure solvent. If the solvent is a strong electron donor, and so able to compete successfully with water for the co-ordination positions of the cation, the heat effect on addition of water to the salt solution is essentially that of addition to the pure solvent. If the solvent is a weak electron donor, the addition can show a net heat effect. Table 3 shows the results of a series of such experiments. For reasons of economy, these measurements were made on solutions resulting from the heat of solution experiments, and therefore differ somewhat in dilution.

Fine distinctions are not possible, particularly among the strongest electron donors, due to a combination of factors, but the ethers as a group are definitely among the strongest donors, the alcohols (with isobutyl alcohol no longer out of place) are possibly less strong, the light-weight ketones come next, and the esters are the weakest electron donors. Comparable results are available for three other salts,[4, 5 or 6] uranyl nitrate dihydrate, cobaltous chloride dihydrate, and cobaltous nitrate dihydrate. A study under controlled conditions and comparable concentrations, and with other

TABLE 3.—HEATS OF REACTION OF 1 MOLE OF WATER WITH THORIUM NITRATE TETRAHYDRATE IN VARIOUS SOLVENTS

Solvent*		ΔH, water to pure solvent (kcal/mole H_2O)	ΔH, water to tetrahydrate solutions (kcal/mole) H_2O)	Net heat evolved (kcal/mole) salt)
Dimethyl formamide	(150)	−0·74	−0·74	0·00
Tetrahydrofuran	(80)	0·51	0·39	0·12
Tributyl phosphate	(80)	0·14	−0·01	0·15
Ethylene glycol diethyl ether	(150)	0·80	0·60	0·20
Diethyl ether	(80)	0·23	0·01	0·22
Isobutyl alcohol	(180)	0·72	0·33	0·39
Ethylene glycol monoethyl ether	(150)	−0·23	−0·76	0·53
Methyl ethyl ketone	(130)	1·30	0·61	0·69
n-Amyl acetate	(200)	0·87	0·09	0·78
Acetone	(80)	0·79	−0·07	0·86
Ethyl acetate	(200)	1·51	0·58	0·93
Ethyl propionate	(150)	1·63	0·46	1·17

* The numbers in parenthesis indicate the solvent/solute mole ratios.

test bases than water, will be necessary to determine whether some of the detailed differences in solvent order with the several salts are an expression of specific interactions.

Nature of the Species in Solution.—The interpretation of the behaviour of thorium nitrate as a solute is complicated by an uncertainty which does not exist for the 2 : 1 salts cited. With the latter, the co-ordination number 6 is clearly established for the cation (4 for cobaltous chloride in some environments), and there is additional evidence that this co-ordination number is maintained with the anions incorporated into the co-ordination sphere when in low-dielectric organic solvents. Therefore, when the dihydrate of one of these salts is used as test material, at least two co-ordination positions clearly remain to be filled by solvent groups, in addition to whatever replacement of water or anions may occur. There is some evidence, as from crystallographic studies of $ThCl_4$, $ThBr_4$, $Th(OH)_2SO_4$, and $Th(OH)_2CrO_4 \cdot H_2O$,[8] that the co-ordination number of thorium may be 8. If this is so, thorium nitrate tetrahydrate already contains sufficient groups to satisfy the co-ordination requirements of the cation. However, the large range of the heat-of-solution effects and the water-acetone and alcohol-acetone mixture results are in complete parallel to the 2 : 1 salt data. Since the heat effects on replacement of water with oxygenated solvent are relatively minor, it is possible that the total co-ordination number of thorium is greater than 8. Another possibility is that there is systematic replacement of at least one of the anions in the thorium co-ordination sphere, and that this gives the basis for the correspondence of the data with those for the 2 : 1 salts. Thus, for example, if in all low dielectric solvents one anion were replaced with a solvent molecule, it might be assumed that

[8] R. C. L. MOONEY, *Acta Cryst.*, **2**, 189 (1949); R. W. M. D'EYE, *J. Chem Soc.*, 2764 (1950); G. LUNDGREN and L. G. SILLÉN, *Arkiv för Kemi*, **1**, 277 (1949); G. LUNDGREN, *ibid.*, **2**, 535 (1950).

the heat effect of separating anion and cation was independent of the solvent, and that the differentiating factor was then the energy with which the replacing solvent molecule is bound to the cation. (For the isobutyl alcohol case, partial replacement of a second nitrate in pure alcohol must be postulated.) The dilution effects noted above might be taken as symptoms of considerable ionic effects, and it should be possible, through comparative electrical conductance measurements, to obtain definitive evidence on this possibility.

Water-Binding Energies.—For the bivalent cations Co^{++} and UO_2^{++} it has been possible to estimate energies with which water is bound to the third and fourth co-ordination positions.[2, 3] With the aid of the above heat-of-solution measurements, it is possible to attempt an estimate of the energy with which water is bound to thorium. Even an order of the magnitude estimate of a water-binding energy for a quadruply charged ion like Th^{4+} would be of value, as there exists no present information of this type.

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As has been shown,[2] with two different hydrates of known formula in hand, for which specific gravities of the solids can be measured and for which heats of solution in water are known, the energy with which the $(m\text{-}n)$ water groups are bound may be estimated. The key calculation is that of the difference in lattice energies of the hydrates, $(U_m\text{-}U_n)$. For 4 : 1 salts there are no calculated Madelung constants as as there are for the 2 : 1 salts. For present purposes one may make use of the fact that, for reasonable packing of atoms, the major component of the Madelung constant is the value of the ionic charges, with detailed arrangements of the ions affecting the value of the constant to a lesser degree. Evidence for this is found by considering the "reduced Madelung constant" A_0 defined by $A = n_1 n_2 A_0 p/_2$ (see, for example, RICE).[9] A is the exact Madelung constant, n_1 and n_2 the ionic charges (1, 2, 3, or 4) and p is the number of ions per molecule. Using the value of A appropriate to the parameter $(\rho/M)^{1/3}$ (see SHERMAN),[10] the A_0 values of the known Madelung constants cluster within about ± 10 per cent of 2·4–2·5, suggesting a value of 24 as an approximation to the Madelung constant for 4 : 1 salts, to be used with the equation [10]

$$U = 279{\cdot}0 \quad A \quad (\rho/M)^{1/3}(1 - 1/n). \tag{1}$$

The water-binding energy E depends on the difference in two lattice energies,[2]

$$(m-n)E = \Delta H_m - \Delta H_n - (U_m - U_n) + (m-n)H_v \tag{2}$$

with the ΔH values being heats of solution of the salts in water, and H_v the heat of vaporization of water.

If one considers the lattice-energy values as single values, the impression is obtained of large, highly uncertain numbers whose difference is completely uncertain. If one takes equation (1) in conjunction with equation (2), however, it is seen that the sources of uncertainty are only the exact value of the difference between the two $(\rho/M)^{1/3}$ values, which is calculable, and the reliability of an average Madelung constant. From the specific gravity values of 2·91 for the tetrahydrate and 2·78 for the pentahydrate (pycnometrically determined in mineral oil and in xylene), the $(\rho/M)^{1/3}$ difference is 0·0041. A change of 0·01 in a specific-gravity value affects

[9] O. K. RICE, *Electronic Structure and Chemical Binding*, McGraw-Hill Book Co., Inc., New York, N.Y., 1940 p. 230.
[10] J. SHERMAN, *Chem. Revs.*, **11**, 93 (1932).

this difference by 0·0002–3, about 5 per cent, so a reliability of 10 per cent in this factor may be assumed. The factor $(1 - 1/n)$ in equation (1) is numerically 0·90 to within one or two per cent.[13] With an assumed 10 per cent reliability of the average Madelung constant, therefore, the lattice energy difference term of equation (2) is probably good to 20 per cent, or ± 5 kcal in the calculated 25 kcal. This gives a water-binding value of (round numbers) 40 $\pm$ 5 kcal for the fifth water bound to thorium.

From the anhydrous thorium nitrate specific gravity of approximately 3·73, a lattice-energy difference from the tetrahydrate of 128 kcal is obtained. A rounded value of 200 kcal for the binding of the first four water groups to thorium, with an uncertainty of perhaps 15–20 kcal, is obtained through substitution in equation (2). The useful reassurance which can be drawn from even such calculations is that there is no order-of-magnitude difference between the binding to Th^{4+} and the divalent cations. For the latter[2] the binding in the third or fourth co-ordination positions is about 34 kcal, and for the first four positions (out of total co-ordination 6) is about 165 kcal.

Acknowledgements— The authors wish to extend sincerest thanks to Dr. DARRELL W. OSBORNE and to Dr. HAROLD R. LOHR for their occasional assistance and for the use of their potentiometer and accessory equipment.

APPENDIX

In earlier calculations[2, 3] of the energy of binding molecular groups to bivalent cations, the values tabulated by SHERMAN[10] for the Madelung constants were used. In particular, with the mean ionic distance equation (based on cube-root of the specific gravity of the solid), the value 6·21 was used for the CdI_2-type crystals. Recalculation since then has shown that this value given by SHERMAN is not consistent with the value given for the calculation through ionic radii. A consistent value for the Madelung constant should be 7·48, about 20 per cent higher than the 6·21 tabulated. All lattice energies for CdI_2-structure halides calculated in the preceding publications[2,3] should therefore be increased by 20 per cent. In general the binding energies calculated from these values will be altered by significantly less than 20 per cent, since heats of solution and heats of vaporization of liquids also enter into the binding-energy calculation. The general conclusions previously drawn are not affected by the revised values for the binding energies, and some of the difficulties in comparing binding of nitrogenous bases and water are eased.

J. Inorganic and Nuclear Chemistry, 1956, Vol. 2, pp. 125–127. Pergamon Press Ltd. London

THE ABSORPTION SPECTRA OF ACIDIFIED MOLYBDATE SOLUTIONS

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(*Received* 16 *July* 1955)

Abstract—It is shown that the absorption spectra of molybdate solutions acidified with nitric acid differ from those shown by molybdate solutions acidified with other mineral acids. This is considered to indicate an interaction between nitrate and molybdate ions in acid solution.

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THE effect of acid concentration on the absorption spectrum of molybdate solutions has been studied by a number of workers.[1–5] It seems to have been generally agreed that it is only the hydrogen-ion concentration which has any effect on the spectrum. The shift of the absorption spectrum towards longer wavelengths, which accompanies an increase in the hydrogen-ion concentration, is due to the increase in the degree of aggregation of the molybdate ions. The anion of the added acid has always been considered to have negligible effect. Interaction between molybdate and nitrate ions is, however, suggested by the anomalous results sometimes obtained in the precipitation of ammonium 12-molybdophosphate for the determination of phosphate,[6] and also by the catalytic action of molybdate on the reduction of nitrate by ferrous iron.[7] In concentrated acid solutions, the existence of cations of hexavalent molybdenum has been postulated;[8] and recently a marked variation in the absorption spectrum of sodium molybdate solutions, with the concentration of the added acid, has been attributed to this type of ion.[5]

All extinction measurements were made, using 10-mm fused silica cells, on a Unicam SP500 spectrophotometer. A hydrogen lamp was used, and for wavelengths greater than 300 mμ the results were reproducible, using instead a tungsten lamp with a blue filter. The absorption spectra in Fig. 1 were confirmed on a Hilger Uvispek spectrophotometer. All solutions were prepared by mixing the appropriate volumes of stock solutions and diluting the mixture to 50 ml in a graduated flask; the blank solutions contained all reagents except molybdate. Interference due to molybdosilicate formation may be considered negligible, since all stock solutions were kept in polythene bottles, and all extinction measurements were made immediately after the preparation of the solutions.

The sodium molybdate stock solution was prepared from laboratory reagent-grade sodium molybdate; the solution was standardized gravimetrically by precipitation of the molybdenum as the oxinate. All acid stock solutions were prepared by dilution of laboratory reagent-grade concentrated acid; the solutions were standardized volumetrically against 0·1 N barium hydroxide. The sodium nitrate stock solution was prepared accurately, using A.R. sodium nitrate.

All pH measurements were made, to an accuracy of 0·05 pH, using a Pye Universal pH meter with a glass electrode and a sodium chloride/calomel reference electrode. To avoid possible crystallization of potassium perchlorate at the tip of the electrode, potassium chloride was not used.

[1] JANDER, G., JAHR, K. F., and HEUKESHOVEN, W. *Z. anorg. chem.*, 1930, **194**, 383.
[2] FREY, H., *Ann. Chim.*, 1943, **18**, 5.
[3] CARPÉNI, G., *Bull. Soc. Chim.*, 1947, **14**, 484.
[4] LINDQVIST, I., *Acta Chem. Scand.*, 1951, **5**, 568.
[5] CHAUVEAU, F., SCHAAL, R., and SOUCHAY, P., *Compt. rend.*, 1955, **240**, 194.
[6] CLARENS, J., *Bull. Soc. Chim.*, 1918, **23**, 147.
[7] KOLTHOFF, I. M., SANDELL, E. B., and MOSKOWITZ, B., *J. Amer. Chem. Soc.*, 1933, **55**, 1454.
[8] LINDQVIST, I., *Acta Chem. Scand.*, 1950, **4**, 650.

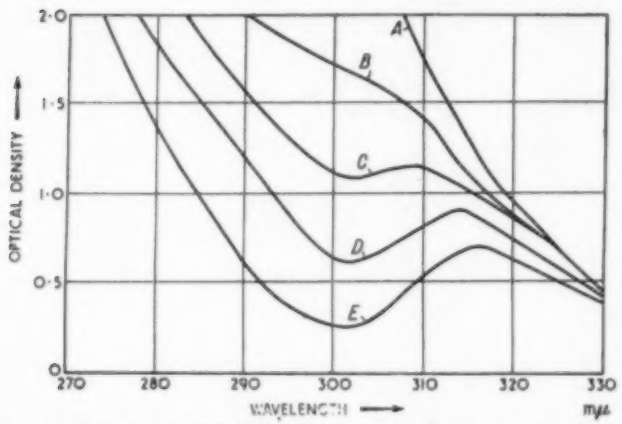

Fig. 1.—The absorption spectra of 0·005 M sodium molybdate solutions in various acid solutions.
A—0·1 N hydrochloric, perchloric, sulphuric, or nitric acid; and 0·5 N hydrochloric, perchloric, or sulphuric acid.
B—0·2 N nitric acid.
C—0·3 N nitric acid
D—0·4 N nitric acid
E—0·5 N nitric acid

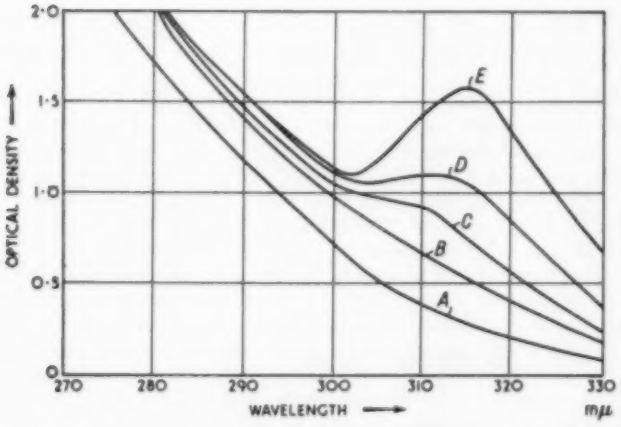

Fig. 2.—The absorption spectra of sodium molybdate in a solution of 0·5 N perchloric acid and 0·3 M sodium nitrate.
A—0·002 M sodium molybdate
B—0·003 M sodium molybdate
C—0·0038 M sodium molybdate
D—0·005 M sodium molybdate
E—0·0075 M sodium molybdate

Fig. 1 shows the absorption spectra of 0·005 M sodium molybdate solutions with added mineral acid. Only in the case of nitric acid is there any deviation from curve *A*, which curve is considered to be the absorption spectrum of 0·005 M sodium molybdate solution at pH < 1. Curves *A*, *B*, *C*, and *D* are reproducible, using 0·5 N perchloric acid and 0·1, 0·2, 0·3, and 0·4 M sodium nitrate respectively; this suggests that the effect is due to the nitrate ions rather than to un-ionized nitric acid. For 0·3 M

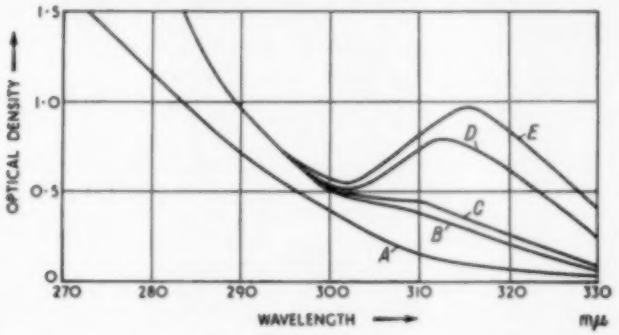

FIG. 3.—The absorption spectra of 0·005 M sodium molybdate in 0·4 M sodium nitrate at different concentrations of perchloric acid.
A—0·001 N perchloric acid (pH 5·0)
B—0·0015 N perchloric acid (pH 4·9)
C—0·002 N perchloric acid (pH 4·8)
D—0·005 N perchloric acid (pH 4·4)
E—0·05 N to 0·5 N perchloric acid (pH < 1·3)

sodium nitrate and 0·5-N perchloric acid the variation in the absorption spectrum of sodium molybdate with concentration is shown in Fig. 2. Fig. 1 and 2 indicate that the deviation increases with increasing concentration of both molybdate and nitrate. Fig. 3 shows that the deviation also increases with increasing hydrogen ion concentration to a constant value for pH < 1·3.

The preceding results indicate some interaction between nitrate and molybdate ions in acid solution. If it is assumed that increased deviation indicates increased interaction, then the interaction between nitrate and molybdate ions is greatest for pH < 1·3, and the law of mass action appears to be applicable to the process.

Acknowledgements—The authors are indebted to the British Rayon Research Association, Manchester, for the use of their Hilger Uvispek spectrophotometer.

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J. Inorganic and Nuclear Chemistry, 1956, Vol. 2, pp. 128–134. Pergamon Press Ltd., London

A TRACER STUDY OF LIQUID PHOSGENE AS AN ACID-BASE SOLVENT*

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(*Received* 5 *April* 1955)

Abstract—Solute aluminium chloride undergoes slow exchange of radiochlorine with liquid phosgene. A solvate of composition $COCl_2 \cdot AlCl_3$ was prepared, and the chlorines of the phosgene and aluminium chloride parts were shown to be non-equivalent. It was found that calcium chloride, sodium chloride, and cesium chloride undergo very little heterogeneous exchange with liquid phosgene.

Ionic chlorides allowed to react with a solution of aluminium chloride do not catalyse exchange of the latter with the solvent. Ionic chlorides undergo reaction by transferring chloride ions directly to aluminium chloride, and not to the solvent as the postulates of the solvent system formulation of acids and bases would require.

It is suggested that: (1) The active agent in aluminium chloride solutions is aluminium chloride itself, not CO^{++} or $COCl^{+}$; (2) The Lewis theory of acids and bases can better be applied to the phosgene solutions than can the theory of solvent systems.

INTRODUCTION

THE solvent properties of liquid phosgene were studied rather extensively by GERMANN and his co-workers.[1] Their work contributed considerably to the development of the solvent systems formulation of acids and bases,[2] which envisages for each solvent a self-ionization comparable to that of water. An "acid" is defined as a solute capable of increasing the concentration of the cations of this self-ionization, while a "base" increases the concentration of the corresponding anions. The protagonists of this formulation have accordingly laid heavy stress on ionic mechanisms for reactions in these solvents.

Recent tracer investigations reported by the author and others[3] have shown that, for the solvents sulphur dioxide and acetic anhydride, ionic mechanisms and analogies to the water system probably have been over-emphasized. It was found, contrary to the postulated[4] ionizations

$$Ac_2O \rightleftarrows Ac^+ + AcO^- \qquad 2SO_2 \rightleftarrows SO^{++} + SO_3^{=}$$

and

$$AcCl \rightleftarrows Ac^+ + Cl^- \qquad SOCl_2 \rightleftarrows SO^{++} + 2Cl^-$$

that there was no rapid exchange either of sulphur between sulphur dioxide and thionyl chloride, or of carbon between acetyl chloride and acetic anhydride. In order better to define the extent to which the solvent system formulation can be applied, we are extending our work to other solvents, the present paper being a preliminary report on phosgene.

* Presented before the Kansas City meeting of the American Chemical Society, March 1954.

[1] GERMANN, A. F. O., and BIROSEL, D. M. (1925) *J. Phys. Chem.*, **29**, 1469, *et ante*.
[2] (a) AUDRIETH, L. F., and KLEINBERG, J. (1953) *Non-Aqueous Solvents*, Ch. 2, Wiley, New York.
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[3] (a) JOHNSON, R. E., NORRIS, T. H., and HUSTON, J. L. (1951) *J. Amer. Chem. Soc.*, **73**, 3052.
(b) EVANS, E. A., HUSTON, J. L., and NORRIS, T. H. (1952) *J. Amer. Chem. Soc.*, **74**, 4985.
[4] JANDER, G. (1949) *Die Chemie in Wasserähnlichen Lösungsmitteln*, Springer-Verlag, Berlin.

EXCHANGE REACTIONS

$AlCl_3$-$COCl_2$ Exchange.—Aluminium chloride is readily soluble in liquid phosgene; GERMANN found that the solution had a greater electrical conductivity than phosgene alone, could dissolve metals with evolution of carbon monoxide, and could be electrolysed to give carbon monoxide and chlorine. Furthermore, such ionic chlorides as sodium chloride, calcium chloride, etc. (which are insoluble in phosgene) are dissolved by aluminium chloride solution. On the basis of these observations he postulated[5] the ionizations

$$COCl_2 \rightleftarrows CO^{++} + 2Cl^-$$

and

$$COCl_2 + Al_2Cl_6 \rightleftarrows CO^{++} + Al_2Cl_8^=$$

The active agent in an aluminium chloride ("solvo acid") solution is then CO^{++}, which is capable of such reactions as:

$$CO^{++}Al_2Cl_6^= + CaCl_2 \rightarrow Ca^{++}Al_2Cl_8^= + COCl_2$$

to give a solution of a "solvo salt."

TABLE 1.—ALUMINIUM CHLORIDE-PHOSGENE EXCHANGE, 0°

	Conc. $AlCl_3$ (Equivalent fraction)	$T^{1/2}$
Light	0·0166	58 hr
Dark	0·0172	59 hr
S/V = 37·8*	0·0046	62 hr
S/V = 4·2	0·0042	59 hr

* Packed with glass rods.

Such solvent-solute interaction would require that chloride ions should be *rapidly* exchanged between aluminium chloride and solvent phosgene. However, it was found in the present work that this exchange is rather slow. Half-times have been observed at 0° ranging from twelve to sixty hours. (The rate is concentration-dependent.) But aluminium chloride solutions react much more rapidly than this with solid ionic chlorides. A sample of sodium chloride sufficient to react with one-half the aluminium chloride present dissolved within thirty seconds. The chlorides of calcium and strontium dissolved more slowly, but in all cases within five minutes.

The exchange reaction is being subjected to a detailed kinetic study, and certain features may be noted at this time. The data in Table 1 indicate that it is homogeneous and non-photochemical.

When conventional plots[6] were made of log (1-fraction exchanged) vs. time, it was found that the straight lines did not intersect the zero-time ordinate at zero exchange. The values of $T^{1/2}$ are corrected for this effect.

[5] GERMANN, A. F. O. (1925) *Science* (3) **61**, 70.
[6] FRIEDLANDER, G., and KENNEDY, J. W. (1949) *Introduction to Radiochemistry*, Wiley, New York, p. 285ff.

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At present it is not possible definitely to explain this effect, but it appears there may be exchange between aluminium chloride and either hydrogen chloride or elemental chlorine impurity in the phosgene, these exchanges being much more rapid than the aluminium chloride-phosgene exchange.[7]

Since the half-time for exchange is concentration-dependent at high concentrations of aluminium chloride (the order with respect to aluminium chloride is greater than 1), all comparisons in this paper are therefore made between runs with nearly equal concentrations, or are made in the low-concentration region where $T^{1/2}$ is roughly independent of concentration.

Aluminium Chloride Solvate.—A compound of formula $AlCl_3 \cdot COCl_2$ can be obtained by distilling off solvent phosgene at dry-ice temperature. Then at room temperature the phosgene of crystallization is easily distilled off *in vacuo*. In accord with the solvent system, this compound could be formulated as $[COCl]^+[AlCl_4]^-$ (as LUDER and ZUFFANTI[2b] designate a solution of aluminium chloride in phosgene), but the phosgene obtained by its thermal decomposition always has a specific activity much less than that of the aluminium chloride, and only slightly greater than that of the solution from which it was crystallized. Therefore, there is no rapid exchange within the solid. The following lists specific activities of (1) aluminium chloride, (2) phosgene of crystallization, and (3) solvent phosgene: (1) 125, (2) 6·29, (3) 5·29; (1) 122, (2) 4·34, (3) 4·16; (1) 210, (2) 3·43, (3) 2·83; (1) 112, (2) 5·77, (3) 5·50. Little is known of compound formation in this system. BAUD[8] reported the preparation of $Al_2Cl_6 \cdot 5COCl_2$, $Al_2Cl_6 \cdot 3COCl_2$, and $2Al_2Cl_6 \cdot COCl_2$, but no $AlCl_3 \cdot COCl_2$. But it appears that BAUD's work connot be entirely reliable. He reported that the latter of his three compounds was stable up to 160°, which is not consistent with easy desolvation of aluminium chloride *in vacuo*. It appears his results may be traceable to absorption of moisture in the open air.

Phosgene—Ionic Chlorides.—We[3] have previously found that sulphites dissolved in liquid sulphur dioxide and acetates dissolved in acetic acid or acetic anhydride all undergo rapid exchange with the solvent. Unfortunately, no ionic chlorides (solvo bases) are known to be soluble in liquid phosgene, and a qualitative investigation during the course of this work disclosed no appreciable solubility for the chlorides of rubidium, cesium, and tetramethylammonium. Since we had [3b] found an appreciable rate of heterogeneous exchange between sodium acetate and acetic anhydride (4·8 per cent in one hour), investigation was made of possible heterogeneous exchanges between phosgene and radioactive chlorides (so prepared as to have high surface area) of sodium, cesium, and calcium. Exchange did take place in each case; but extremely slowly. There are listed (1) time in days and (2) per cent exchange, all runs being made at 25·0°:

For $CaCl_2$	(1) 15·8,	(2) 0·11;	(1) 119,	(2) 0·27.
For NaCl	(1) 0·9,	(2) 0·16;	(1) 45·8,	(2) 1·06;
	(1) 113,	(2) 1·06		

[7] (a) The effect is increased by adding either hydrogen chloride or chlorine, and decreased by fractionation of the phosgene (as described in the experimental section) until its vapour pressure is reduced to a constant value.
(b) The effect is greatest for low aluminium chloride concentrations, and lowest for high concentrations.
(c) If radioactive phosgene obtained by distillation from aluminium chloride at the end of the run is fractionally distilled, the last fraction always has a lower specific activity than that of the first fraction.

[8] BAUD, G. (1905) *Compt. Rend.*, **140**, 1688.

While these results must be interpreted with caution, it is obvious that this indication of the "inert" character of phosgene as a solvent is in line with the rest of this work; that is, there can be little self-ionization. Indeed, the slowness of these heterogeneous exchanges is striking, since WALLACE and WILLARD[9] found a rapid heterogeneous exchange between aluminium chloride and carbon tetrachloride, the latter of which is generally considered to be an "inert" solvent. (They proposed the adsorption of polarized carbon tetrachloride molecules on the ionic crystal lattice as the mechanism for their exchange.)

Phosgeno-Aluminates.—As previously stated, GERMANN prepared a number of compounds between aluminium chloride and various ionic chlorides, which compounds he designated as phosgeno-aluminates. Of these the calcium salt was the most thoroughly studied: $CaCl_2 \cdot 2AlCl_3 \cdot 2COCl_2$[10], which can be formulated as a salt with phosgene of crystallization, $CaAl_2Cl_8 \cdot 2COCl_2$. Similar compounds were made from sodium chloride, strontium chloride, and barium chloride.[11]

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Since we have found[12] that ionic halides exert a powerful catalytic effect on the rate of exchange of sulphur between thionyl chloride and sulphur dioxide, the phosgene-aluminium chloride system was investigated for a similar effect. Radioactive aluminium chloride (in excess of the stoichiometric quantity required for reaction) was dissolved in phosgene which was already in contact with anhydrous inactive calcium chloride or sodium chloride. The calcium chloride or sodium chloride dissolved within a few minutes, but produced no catalysis. In Table 2 observed half-times are compared with estimations from other runs of what the half-times would have been had no ionic chloride been present. No high accuracy can be claimed for this estimation, but it is striking that the half-time in the presence of ionic chloride is never less than these estimated half-times.

Since there is no catalysis, it becomes possible to make a direct tracer test of GERMANN'S postulate that CO^{++} is the active agent in dissolving calcium chloride. For if we use Cl—radioactive calcium chloride, its activity would be *immediately* transferred to the solvent by the process $CO^{++} + 2Cl^- \rightarrow COCl_2$. But it can be seen that this does not take place to any great extent: the zero-time intercepts of log $(1 - F)$ vs. T plots listed in Table 2 set upper limits to the percentage of ionic chloride dissolved by this mechanism. These small quantities are, or course, contributed to by any exchange of aluminium chloride with chlorine or hydrogen chloride impurity.

Certain other features of these experiments may be noted:

Chloraluminate ion (perhaps $AlCl_4^-$) seems to be less active kinetically than aluminium chloride towards exchange with solvent phosgene, this being especially marked in Runs 3, 4, and 7. (Runs 1 and 2 are in the concentration-independent region.) On the other hand, there is no significant difference in the rates of exchange obtained from duplicate experiments in one of which the aluminium chloride is labelled, and in the other the "base." It seems safe to assume, then, that chloride is rapidly exchanged between aluminium chloride and the chloraluminate ion formed from it. The rate of exchange found in the sodium chloride experiments is significantly greater than in the calcium chloride or strontium chloride experiments, and there

[9] WALLACE, C. H., and WILLARD, J. E. (1950) *J. Amer. Chem. Soc.*, **72**, 5275.
[10] GERMANN, A. F. O., and TIMPANY, C. R. (1925) *J. Phys. Chem.*, **29**, 1423; *J. Amer. Chem. Soc.*, (1925) **47**, 2275 and (1925) **47**, 2461.
[11] GERMANN, A. F. O., and BIROSEL, D. M. (1925) *J. Phys. Chem.*, **29**, 1469.
[12] HERBER, R. H., NORRIS, T. H., and HUSTON, J. L. (1954) *J. Amer. Chem. Soc.*, **76**, 2015.

is a lesser difference (of dubious significance) between the strontium chloride rate and the comparable calcium chloride rate. Perhaps these differences have to do with intensity of electrical field, e/r, around the cation. Unfortunately, the indicated experiments with potassium chloride and cesium chloride resulted in insoluble products and of course very slow rates of exchange. Barium chloride produced a lower, salt-rich phase (noted by GERMANN[11]) which soon crystallized, giving again slow exchange.

The slowness of the exchange of chloride between aluminium chloride and solvent phosgene should not be taken to mean that there are no ionic species present in the

TABLE 2.—FORMATION OF PHOSGENO-ALUMINATES

Run	Reactants	Conc., $AlCl_3$ Initial	Equiv. Fraction $AlCl_3$* Residual	$T^{1/2}$ hrs. Observed	$AlCl_3$ alone	Zero-time Intercept Per cent †
1	$AlCl_3^{\neq} + CaCl_2$	0·0176	0·0113	59	54	—
2	$AlCl_3 + CaCl_2^{\neq}$	0·0163	0·0104	62	54	8
3	$AlCl_3^{\neq} + CaCl_2$	0·0359	0·0160	73	39	—
4	$AlCl_3 + CaCl_2^{\neq}$	0·0402	0·0193	72	37	5
5	$AlCl_3^{\neq} + NaCl$	0·0368	0·0167	39	37	—
6	$AlCl_3 + NaCl^{\neq}$	0·0370	0·0169	41	37	3
7	$AlCl_3 + SrCl_2^{\neq}$	0·0381	0·0181	62	38	6
8	$AlCl_3 + BaCl_2^{\neq}$	0·0374	0·0175	175	38	6

(*) Assuming the reaction stoichiometry is $AlCl_3 + Cl^- \rightarrow AlCl_4^-$
(†) Maximum per cent of solid chloride reacting by $CO^{++} + 2Cl^- \rightarrow COCl_2$

solution, for certainly the conductivities measured by GERMANN were real. But it seems certain that self-ionization of the solvent is of little or no significance. The slowness of the exchange, the non-equivalence of chlorine atoms in the solvate $COCl_2 \cdot AlCl_3$, as well as its ready decomposibility, all indicate that forces of interaction between aluminium chloride and phosgene molecules are weak by comparison to the bonds within each.

It would follow, of course, that substantial activation energy could be needed to accomplish the transfer of a chloride ion from its covalently bound position in a phosgene molecule to a similarly covalently bound position in a chloraluminate ion. The rapid exchange between aluminium chloride and chloraluminate ion may be explained, somewhat formally, as taking place *via* the ionization.

$$Al_2Cl_6 \rightleftarrows AlCl_2^+ + AlCl_4^-$$

In summary, then:

1. There is no evidence that self-ionization plays a significant part in phosgene-solution chemistry.
2. Aluminium chloride dissolves in phosgene and ionizes only slightly with slow exchange of chloride ions.
3. Aluminium chloride in phosgene solution is a good chloride ion acceptor. The reaction of aluminium and calcium chloride consists of the transfer of chloride ions directly from the latter to the former.

4. The reactions of aluminium chloride may be interpreted as acid-base phenomena in terms of the Lewis theory, on the assumption that aluminium chloride is an acceptor for chloride ions, and that the phosgene molecule may be a moderate electron-pair donor. The initial "neutralization" to form an aluminium chloride-phosgene complex may be rapid, but the actual transfer of a chloride ion involves the breaking of strong carbon-chlorine bonds, and has an appreciable activation energy.

EXPERIMENTAL

Phosgene.—Matheson tank phosgene was used. Since this is stated by the manufacturer to be 99·9 per cent pure, it was used in preliminary runs without purification. After the effect of small amounts of hydrogen chloride and chlorine was discovered, the tank material was condensed in a trap at 0°, and some was then boiled away until the 0° vapour pressure had fallen to 555 mm (the lowest value reported by GERMANN). About one-fourth more was boiled away, and about two-thirds of the residue evaporated into the gas-handling system to be stored behind a Stock valve.

Radiochlorine.—This was obtained from Atomic Energy of Canada, Ltd. as dilute HCl. This was vacuum-distilled once.

Aluminium Chloride.—Silver chloride was converted into aluminium chloride by reaction above its melting-point with 30-mesh aluminium metal *in vacuo*. To free it of any traces of unreacted silver chloride, it was sublimed through hot aluminium and condensed in a spiral at room temperature. This spiral was open to high vacuum during the condensation, the purpose being to free the aluminium chloride of any traces of radioactive hydrogen chloride. It was finally sublimed into a number of small, fragile ampoules, somewhat after a procedure previously used for acetic acid and acetic anhydride.[3b] The same procedure was used to prepare both active and inactive material.

C.P. calcium chloride was recrystallized once and a solution was standardized by titration. The chlorides of sodium, strontium, cesium, and barium, were C.P. or reagent grades, used without purification.

RUN PROCEDURES

When it was desired to take samples rapidly after aluminium chloride and phosgene had been brought together, an apparatus was used which was based on one shown as Fig. 1 in EVANS *et al.*[3b] This apparatus consisted essentially of a chamber so provided with stopcocks and ground joints as to allow the collection of phosgene samples by evaporation into a volume of adjustable size, and their removal from the apparatus by liquid-air distillation. To start a run, one of the aluminium chloride ampoules was placed in the chamber and, after evacuation, phosgene was distilled in. After bringing to the proper temperature (usually 0°) the ampoule was broken by manipulating, via a ball-and-socket ground joint, a glass pestle inside the chamber.

When it was not desired to take samples rapidly and it was not necessary to know the zero-time with great accuracy, the aluminium chloride and phosgene were simply brought together by liquid-air distillation, after smashing the ampoule *in vacuo* with a glass-breaker. By weighing the ampoule beforehand and the glass fragments remaining, it was possible to adjust the amount of phosgene to be introduced and thus the concentration of the solution.

When ionic chloride was to be allowed to react with aluminium chloride, the

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former was introduced first into the apparatus as aqueous solution and acidified with hydrochloric acid, the latter being radioactive if desired. After vacuum sublimation to dryness and, when hydrates were involved, dehydration, the part of the apparatus containing the salt was flamed, and then the second procedure given above for ordinary runs was followed.

Phosgene was measured out in a bulb of known volume fitted with a manometer, but the amount introduced and amount removed at the end of a run were always determined by weighing in a small container fitted with a pressure stopcock. Phosgene alone was handled with stopcocks greased with Apiezon-N; some dissolved in the grease but there was no evidence of reaction. However Apiezon-N could not be used on stopcocks near a phosgene solution of aluminium chloride. It was invariably attacked—by spray, presumably. Such stopcocks were lubricated with high-vacuum silicone grease, with a ring of apieson applied at each end to prevent striation and leakage. In such apparatus the same results were obtained as in all-glass apparatus. Halocarbon grease was found to absorb undue amounts of phosgene vapour.

Counting.—In early runs the samples of phosgene were hydrolysed and their chlorine assayed as mercurous chloride. (This was always done for aluminium chloride.) In most runs, however, phosgene vapour was counted as such in a double-walled solution counter similar to one used by WALLACE and WILLARD,[9] but obtained from ECK and KREBS. A manometer with a mercury levelling bulb attached at its bottom permitted compensation during counting for a slight tendency for the phosgene to dissolve in stopcock grease, with consequent pressure diminution. After counting, the samples were not destroyed but were returned to the phosgene-aluminium chloride solution. Transfer of the samples was by liquid-air distillation.

The solvate obtained at the end of the runs by distillation at dry-ice temperature was analysed many times. Phosgene of crystallization was pumped off at room temperature, hydrolysed, and its chloride titrated mercurmetrically. Residual aluminium chloride (whether or not taken through the solvate stage) was also hydrolysed and analysed by similar titration, and by precipitation of aluminium as the 8-hydroxyquinolate. Typical data are as follows: For aluminium chloride, $AlCl_{3\cdot01}$; for the solvate, $AlCl_3 \cdot 0{\cdot}99\ COCl_2$.

Acknowledgement—This work was supported by the U.S. National Science Foundation.

Powder Data for ThF_4, 0·5–2·0 H_2O

(*Received* 28 *October* 1955)

In a recent paper, D'Eye and Booth[1] index the powder data for ThF_4, 0·5–2·0 H_2O on the basis of an orthorhombic unit cell. They quote the following systematic absences

hkl present only when $h + k + l = 2n$		(i)
*hk*0 present only when $h = 2n$	($k = 2n$)	(ii)
*h*0*l* present only when $h = 2n$	($l = 2n$)	(iii)
0*kl* present only when $k = 2n$	($l = 2n$)	(iv)
*h*00 present only when $h = 2n$		(v)
0*k*0 present only when $k = 2n$		(vi)
00*l* present only when $l = 2n$		(vii)

from which they deduce the space group to be $I2_12_12_1$ and then discuss a possible distribution of the sixteen thorium atoms in four sets of four-fold special positions.

The argument is, however, unsound.

The absences (i), (v), (vi), and (vii) are all covered by the body-centred condition, and leads to the Buerger diffraction symbol *mmmI* . . . , which in turn leads to a choice of four possible space groups, namely *I*222, $I2_12_12_1$ (which pair contains the same number of diads and screw diads), *Imm*2, and *Immm*. If the absences (ii), (iii), and (iv) are exact, the diffraction symbol becomes *mmmIbca*, which uniquely fixes the space group as *Ibca*.

It is unlikely that the space group is either *I*222, *Imm*2, or *Immm*, as then the absences (ii), (iii), and (iv) would have to arise by chance, irrespective of whether the thorium atoms are in general or special positions. With $I2_12_12_1$, these absences arise for atoms distributed in the four-fold special positions related by the three pairs of diads, but for the absences to be exact the fluorine atoms would also have to be distributed in sixteen sets of these four-fold positions, and this would give rise to absurd packing.

With *Ibca*, however, the thorium atoms may be distributed in the sixteen general positions or on the eight-fold positions of symmetry 2 or $\bar{1}$. These positions would confer additional absences (applicable to the thorium-atom contributions only) which would cause the general *hkl* reflections to be weak when *h*, *k*, or *l* is odd, dependent upon the choice, and as 211 is called "strong," 132 "medium," and 112 "medium," this would not appear to be the case.

On their data, it may thus be deduced that the probable space group is *Ibca*, with the sixteen thorium atoms distributed in general positions.

O. S. Mills

Department of Chemistry,
University of Sheffield

[1] R. W. M. D'Eye and G. W. Booth, *J. Inorg. Nucl. Chem.*, **1**, 326 (1955).

Powder Data for ThF_4, 0·5–2·0 H_2O

(*Received* 8 *November* 1955)

I agree with Dr. Mills that if the absences:

*hk*0 present only when $h = 2n$	($k = 2n$)
*h*0*l* present only when $h = 2n$	($l = 2n$)
0*kl* present only when $k = 2n$	($l = 2n$)

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are exact, then the space group would be *Ibca*. I also agree that if these absences are exact, then with the space group $I2_12_12_1$ the fluorine atoms would be distributed on sixteen sets of four-fold positions, which is extremely improbable.

However, it is likely that these absences are not exact, due to the low scattering power of the fluorine and the rather poor photographs. If this is the case, then the thorium atoms will be on four-fold special positions and the fluorine atoms on the eight-fold general position of $I2_12_12_1$.

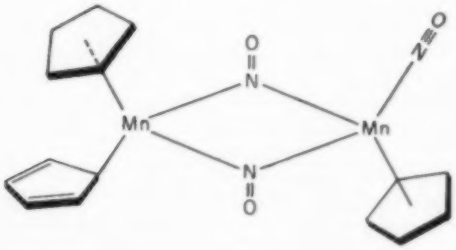
Atomic Energy Research Establishment,
Harwell, Didcot, Berks.

R. W. M. D'EYE

Erratum

T. S. PIPER and G. WILKINSON, Cyclopentadienyl-nitric oxide compounds of chromium and manganese, *J. Inorg. Nucl. Chem.*, *2*, 42 (1956)—

The correct version of Fig. 1 (b) is as follows—



(b)

Fig. 1 (b), as previously published, was an example of a less satisfactory model.—G. W.

J. Inorganic and Nuclear Chemistry, 1956, Vol. 2, pp. 137–140. Pergamon Press Ltd., London

AN ELECTRONIC INTERPRETATION OF THE *TRANS* EFFECT IN PLATINOUS COMPLEXES

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(*Received* 25 *October* 1955)

Abstract—It is shown that the lability of groups *trans* to double bonding ligands in planar platinous complexes can be understood in terms of crystal-field or molecular-orbital theory if a simple configuration for the transition state is assumed.

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IT has been known for many years that there are certain ligands which tend to labilize the groups *trans* to themselves in planar divalent platinum complexes. The experimental evidence on this and some closely related topics has been reviewed by QUAGLIANO and SCHUBERT.[1] More recently the importance in transition-metal chemistry of double-bonding using metal d_π orbitals has been emphasized by a number of authors,[2, 3, 4] and CHATT, in particular, has discussed this aspect of the electronic structure of platinum complexes with reference to the *trans* effect. In this paper we shall propose a more detailed electronic interpretation of the *trans* effect, which may be based on crystal-field theory or on the almost equivalent molecular-orbital theory.[5, 6]

The experimental evidence on the *trans* effect may be summarized briefly as follows:

(1) The different ligands which can occur in platinous complexes have very different effects on the lability of the groups *trans* to themselves. A sequence of ligands in order of increasing *trans* effect is

$$H_2O < OH^- < NH_3 \sim F^- < Cl^- < Br^- < I^- \sim R_3P \sim R_2S < SC(NH_2)_2 < NO_2^- < CO \sim C_2H_4 < CN^-.$$

It has been pointed out that the ligands with the largest *trans* effects are just those which have vacant orbitals suitable for forming π-bonds.[2]

(2) In the substitution reactions of platinous complexes of the type which we have to consider, the stereochemical configuration is maintained, that is in a reaction

$$Pt^{II}\,ABCD + E \rightarrow Pt\,ABCE + D$$

the replacement of D by E occurs without any change in the relative positions of A, B, and C.

Our first problem is to decide which is the most likely transition state for these replacement reactions. It seems almost certain that many of the reactions are second

[1] J. V. QUAGLIANO and L. SCHUBERT, *Chem. Rev.* **50**, 201 (1952).
[2] J. CHATT and A. A. WILLIAMS, *J. Chem. Soc.* 3061 (1951).
[3] D. P. CRAIG, A. MACCOLL, R. S. NYHOLM, L. E. ORGEL, and L. E. SUTTON, *J. Chem. Soc.* 332 (1954).
[4] F. H. BURSTALL and R. S. NYHOLM, *J. Chem. Soc.* 3570 (1952).
[5] L. E. ORGEL, *J. Chem. Soc.* 4756 (1952).
[6] L. E. ORGEL, *J. Chem. Phys.* **23** (1955). In press.

order, for otherwise fairly rapid equilibration of mixtures of *cis* and *trans* isomers would be expected, e.g.,

$$\underset{cis}{Pt^{II}A_2BC} \rightleftharpoons Pt^{II}ABC + A \rightleftharpoons \underset{trans}{Pt^{II}A_2BC}.$$

If this is correct, the transition state must involve five-co-ordinated platinum. The more usual configurations for five-co-ordinated metal complexes are not consistent with the evidence quoted in (2), for the latter implies that in the transition state, e.g., of an isotopic substitution reaction, the entering and leaving groups are equivalent to each other but not to any other groups and, furthermore, the distinction between the groups *cis* and *trans* to the reacting group is maintained. The only simple configuration having the required properties is shown in Fig. 1.

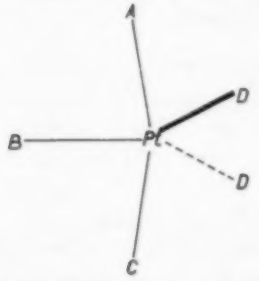


FIG. 1.—Proposed distorted bipyramid structure for the transition state.

Our picture of the reaction path is thus roughly as follows. The entering group approaches the complex ion from one side of the plane and in the critical stage of the reaction moves over the group to be replaced and then downward until the transition state is reached. The replaced group is then eliminated by an equivalent process.

This reaction mechanism has not been confirmed definitely by experiment. It has the following features which recommend it:

(a) It is the simplest mechanism which can be suggested and is quite closely related to the edge-displacement mechanism recently proposed for substitution reactions of octahedral complexes.[7]

(b) It is consistent with the experimental evidence in (2).

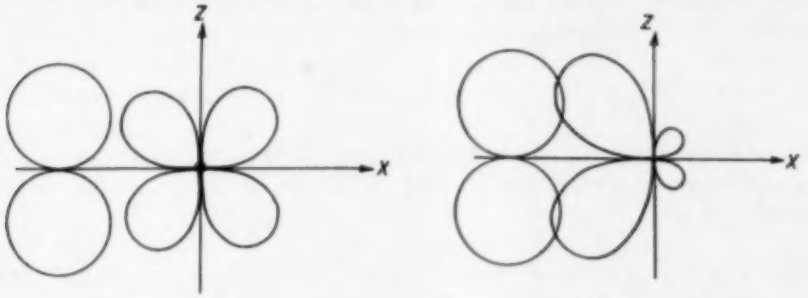
(c) It allows one to give a very simple electronic interpretation of the *trans* effect. We shall assume that the transition state suggested in Fig. 1 is the correct one.

The crystal-field and molecular-orbital theories both lead to the conclusion that the condition necessary for the stability of a given geometric configuration of a complex is that in that configuration the *d*-electrons of the metal ion must be able to avoid the region of maximum concentration of the ligand electrons. This criterion can be applied to the case of our proposed transition state, and leads to the conclusion that any process which reduces the *d*-electron concentration along the Pt–*D* and Pt–*D** directions must stabilize the transition state and hence increase the lability of the complex.

If we choose a co-ordinate system such that the Pt, *D* and *D** groups lie in the *xz* plane and the Pt, *A*, *B*, and *C* groups in the *xy* plane, there is just one *d* orbital,

[7] D. D. BROWN, C. K. INGOLD, and R. S. NYHOLM, *J. Chem. Soc.* 2674 (1953).

the d_{xz} orbital, which has its maximum concentration along the critical directions. This orbital is furthermore just the one which is required for double bonding with the group *trans* to the reacting group, but which is unable to bond to groups *cis* to it. We have already seen that the groups with large *trans* effects are those which have vacant π-orbitals capable of accepting metal *d*-electrons through double bonding, i.e., they are the groups which might be expected to reduce the *d*-electron density along the Pt–*D* and Pt–*D** directions in the transition state. We have thus provided a detailed qualitative interpretation of CHATT's suggestion that the *trans* effect depends on the ability of the directing group to form a double bond with the metal ion.



(a) (b)

FIG. 2.—The critical *xz* orbital: (a) without hybridization, (b) with hybridization.

In Fig. 2(a) we have shown diagrammatically the critical π-orbital in the five-co-ordinated transition state. The electron density along the Pt–*D* and Pt–*D** directions has been reduced from that for a complex in which the *trans* group cannot form double bonds by the spreading of the d_{xz}-orbital onto the ligand *B*. In fact we believe that d_π–p_π hybridization of the kind proposed on theoretical grounds by CRAIG and co-workers,[3] and discussed in detail by CHATT[8] with reference to the platinum-olefine complexes, is important. In Fig. 2(b) we show the critical orbital after such hybridization has been taken into account. It should not be thought that d_π–p_π hybridization takes place only if the group *B* has vacant π-orbitals. While this may be true for planar complexes, the highly asymmetric field in the transition state must always cause extensive d_π–p_π mixing. The presence of empty orbitals on *B* merely reduces the energy required to reach the transition state.

There is a second feature of the electronic structure of the ligand which may affect the stability of the transition state. If a ligand is a poor σ-electron donor, then the $5d_{z^2-y^2}$, 6*s*, and 6*p* orbitals of the metal tend to be less occupied than otherwise, and so are more readily available for the formation of an extra partial σ-bond in the transition state. This effect should have a large non-directional component, i.e., it should make *cis* groups almost as labile as *trans* groups. Since this is contrary to almost all of the experimental findings, we do not believe the σ effect to be large. It may, however, reinforce the more important double bonding effect, e.g., in carbon monoxide complexes.

The mechanism which we have proposed is applicable to the reactions of other planar complexes formed by metal ions with eight *d*-electrons, e.g., Pd^{++}, Ni^{++}, and

[8] J. CHATT (1953), Symposium on Co-ordination Chemistry, Copenhagen. Published by the Danish Chemical Society.

Au^{+++}. In the case of nickel, however, it is quite likely that in some reactions a different mechanism is involved, namely the conversion of the planar complex to an octahedral one followed by elimination of two groups.

The reaction mechanism which we have proposed involves a transition state whose geometry is closely related to that of the trigonal bipyramid structure to be expected for five-co-ordinated complexes with eight *d*-electrons. Exactly equivalent bonds are not to be anticipated in general (see Fig. 1), but if the directing group, the replaced group, and the reagent are identical, then the transition state should be a ***regular*** trigonal bipyramid. This raises the general question of the stability of such structures and suggests that if any of them are stable they should occur with strongly π-bonding ligands. The fact that replacement reactions occur quite rapidly at room temperatures shows that, provided the reactions are second-order, the reaction to form a five-co-ordinated complex cannot be endothermic by much more than 20 kcal.

Note added in proof—Since this paper was submitted for publication, a closely related paper by CHATT and VENANZI (*J. Chem. Soc.*, in press) has come to the author's notice.

Acknowledgement—The author is indebted to J. S. GRIFFITH for a helpful discussion.

J. Inorganic and Nuclear Chemistry, 1956, Vol. 2, pp. 141–148. Pergamon Press Ltd., London

SPECTRA AND STRUCTURES OF METAL-CARBON MONOXIDE COMPOUNDS—II*

MANGANESE AND RHENIUM DECACARBONYLS

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(*Received* 14 *September* 1955)

Abstract—The infra-red absorption spectra of $Mn_2(CO)_{10}$ and $Re_2(CO)_{10}$ have been measured from 450-3000 cm^{-1} in the solid, in solution, and in the gas phase.

The spectra are interpreted according to a method of local symmetry, and two possible structures, both involving a pseudo-ring of carbon monoxide ligands lying between the metal atoms, are suggested.

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1. INTRODUCTION

IN a previous note[1] we have analysed the infra-red spectra of several cyclopentadienyl-carbon monoxide derivatives of transition elements to obtain the general features of the structure of these compounds. Using what may be called a *method of local symmetry*, it was shown how the number of structural possibilities could be drastically limited by observation of the number and positions of carbon-oxygen stretching frequencies. In this method, it is assumed that selected portions of a complex molecule may be treated as isolated units; that is to say, that their interactions with other parts of the molecule may be ignored. To determine the activities of the vibrations of such a subgroup of atoms, only the *local symmetry* of this subgroup need then be considered.

It seemed possible that these principles developed for the cyclopentadienyl-carbon monoxide metal compounds could be applied to the polynuclear metal carbonyls, and in this paper we have attempted to analyse the spectra of manganese and rhenium carbonyls along these lines. Before proceeding further, it seems appropriate in connection with the method of local symmetry to note some empirical but seemingly well-established generalizations concerning the frequencies at which several types of CO groups occurring in metal-carbon monoxide compounds absorb in the infra-red.

The following types of carbonyl groups may be distinguished.

1. *Simple CO groups.* This type of CO group exists (a) in the mononuclear metal carbonyls such as $Cr(CO)_6$, $Ni(CO)_4$; (b) in the mononuclear cyclopentadienyl-carbon monoxide metal compounds such as $C_5H_5Mn(CO)_3$, $C_5H_5Co(CO)_2$; (c) in what may be called "terminal" or "end" groups, i.e., non-bridging groups, in binuclear metal carbonyls, as, for example, in the six end-groups of iron enneacarbonyl $(CO)_3Fe(CO)_3Fe(CO)_3$; (d) in complexes such as $K_3[Fe(CN)_5CO]$.

It appears certain that such CO groups bound to only one metal atom absorb at ~2000 cm^{-1}, without an exception known to us, between 1910 cm^{-1} and 2060 cm^{-1}.

2. *Ketonic bridging CO groups.* There is considerable evidence and reason for

* Paper I in this series is reference (1).
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(1) F. A. COTTON, A. D. LIEHR, and G. WILKINSON, *J. Inorg. Nucl. Chem.* **1**, 175 (1955).

believing[1, 2, 3] that in certain polynuclear metal carbonyls, particularly $Fe_2(CO)_9$ and $Co_2(CO)_8$, there are CO groups which function as "ketonic" bridges between two metal atoms, and hence absorb at frequencies characteristic of sterically similar ketone groups in organic molecules, i.e., 1700–1900 cm^{-1}. A CO group of this type is found also in $C_5H_5Fe(CO)_4Fe\,C_5H_5$.[1]

3. *Non-ketonic bridging groups.* In the binuclear cyclopentadienyl-carbon monoxide compounds, e.g., $C_5H_5W(CO)_6WC_5H_5$, no ketonic CO stretching frequencies were observed, and it was suggested[4] that here bridging is affected by CO groups forming a kind of loosely-bonded pseudo-ring, from which electron density was contributed to the metal atoms, with the bonding both in the ring and from the ring to the metal atoms being more or less delocalized. This suggestion was made to resolve the question of how CO groups could join two metal atoms giving a binuclear molecule, and yet not be of an essentially ketonic nature; for the C-O absorption in these compounds[1] is between 1890 and 1960 cm^{-1}, overlapping the range for simple non-bridging groups.

The recent work by BRIMM, LYNCH, and SESNY[5] on manganese and rhenium carbonyls, $Mn_2(CO)_{10}$ and $Re_2(CO)_{10}$, showed that in spite of the binuclear nature of the compounds, no ketonic bridging carbonyl absorption was observed. A closer examination of the spectra in connection with the present work confirms this observation, and the following analysis suggests that pseudo-ring structures are reasonable for these molecules, and further, that the delocalized mode of bonding of carbon monoxide groups may be of general occurrence.

2. EXPERIMENTAL

We are deeply indebted to Dr. E. O. BRIMM of the Linde Air Products Co., Tonawanda, N.Y., for gifts of the metal carbonyls.

Spectra were taken on a Perkin-Elmer double-beam recording infra-red spectrophotometer Model 21 in the region 3000–650 cm^{-1}, using sodium chloride optics. The region from 650–450 cm^{-1} was studied using a Perkin-Elmer single-beam instrument, Model 12c, coupled with a Brown recorder, using either potassium or cesium bromide optics. Solutions were run in the usual manner, using cells with 0·4-mm spacers and fitted with appropriate halide windows.

The gas-phase spectra were obtained using a cell constructed by Dr. LOUIS LINDEMAN of this laboratory. This hot cell consists of an ordinary gas cell of 4-cm path-length with halide windows cemented on with Glyptal clear varnish No. 1201 (General Electric Co.). This resin was then cured by heating overnight at 130–150°. It is essential always to heat and cool the cell very slowly once the cement has been cured, to avoid cracking the halide windows. The heating jacket consisted of two sections of close-fitting brass tube wound with nichrome wire and covered with asbestos tape. These slip over the cell and are held by springs. The jacket projects about 3 cm beyond each end of the cell and is covered at each end by halide windows loosely bound to the asbestos board end-pieces of the heating jacket. The windows of the cell are in this way kept as hot as the centre portion, and condensation of material on the windows is avoided.

For the vapour-phase studies the cell was maintained at 100–150°C. While quantitative vapour-pressure data are lacking for these substances, the pressures were doubtless of the order of a few millimetres.

3. DATA AND ANALYSIS

The infra-red absorption spectra of $Mn_2(CO)_{10}$ and $Re_2(CO)_{10}$ were studied in the range 450–3000 cm^{-1}. The spectra in the C-O stretching region, 1700–2200 cm^{-1}, are

[2] SHELINE, R. K. and PITZER, K. S., *J. Amer. Chem. Soc.* **72**, 1107 (1950).
[3] CABLE, J. W., NYHOLM, R. S., and SHELINE, R. K., *ibid.* **76**, 3375 (1954).
[4] WILKINSON, G., *ibid.* **76**, 209 (1954).
[5] BRIMM, E. O., LYNCH, M. A., and SESNY, W. J., *ibid.* **76**, 3831 (1954).

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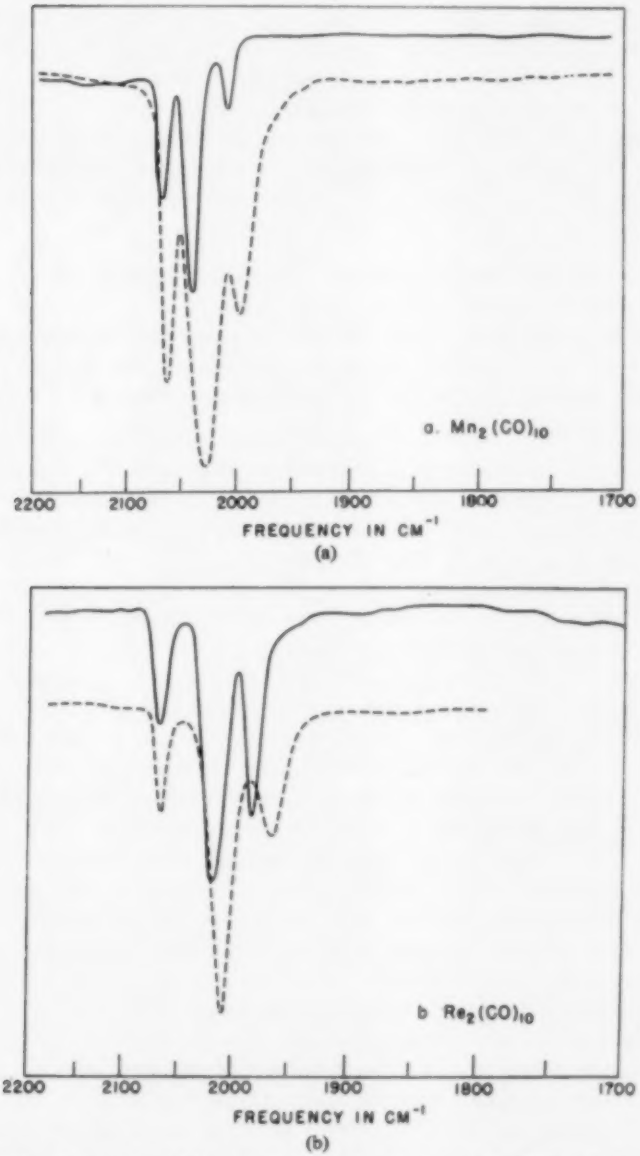

FIG. 1.—Carbonyl stretching spectra in gas phase (——) and in $CHCl_3$ solution (– – –).
(a) $Mn_2(CO)_{10}$: gas at ~120°; solution, ~0·5 mg per ml $CHCl_3$.
(b) $Re_2(CO)_{10}$: gas at ~140°; solution, ~1 mg per ml $CHCl_3$.

shown in Fig. 1, and the principal absorption bands are listed in Table 1. In both compounds there are only three frequencies, all very strong, in the neighbourhood of ~2000 cm^{-1}, and no absorption between 1700 cm^{-1} and 1900 cm^{-1}.[6]

[6] The spectra of BRIMM, LYNCH, and SESNY[5] showed three strong bands in the C-O stretching region but also a weak shoulder at longer wavelengths in each case. No evidence of these shoulders was found in this study.

In view of the absence of ketonic bridging frequencies in $Mn_2(CO)_{10}$ and $Re_2(CO)_{10}$, Brimm, Lynch, and Sesny suggested that the binuclear nature is attributable to a metal-metal bond. The only other reasonable alternative is that, between the metal atoms, there is a pseudo-ring of carbon monoxide groups.

Before applying the method of local symmetry to the problem of $Mn_2(CO)_{10}$ and $Re_2(CO)_{10}$, a brief résumé of the assumptions of the method seems apposite. The validity of the method of local symmetry depends on the fulfilment of the following assumptions:

(a) that a molecule can be resolved into relatively non-interacting vibrating groups,

(b) that due to the small interaction of such groups, the selection rules of the *isolated* groups will be valid for the group when it is non-isolated, i.e., when it is in the molecule, irrespective of the symmetry of the whole molecule.

The groups chosen in (a) are usually those of highest symmetry. This allows one to use group theory in determining the appropriate selection rules. If a molecule contains several equivalent subgroups, we assume that, due to the weakness of the vibrational interactions, the frequencies due to each of these equivalent clusters will be identical.

For the various models for $Mn_2(CO)_{10}$ and $Re_2(CO)_{10}$ to be considered below, it is convenient to adopt a notation descriptive of the arrangement of CO groups. The most general model for any binuclear carbonyl would be represented by (x-y-z), where x and z denote the numbers of terminal simple CO groups bound to only one metal atom, and y denotes the number of CO groups placed between the metal atoms. No geometry or symmetry is implied by such a designation.

For $Mn_2(CO)_{10}$ and $Re_2(CO)_{10}$, only models in which $x = z$ need be considered, since any model with $x \neq z$ would necessarily show more than three C-O bands. The first models to be considered, which are several containing metal-metal bonds and therefore designated (5-0-5) models, serve to illustrate the notation.

In Table 2 the results of applying the method of local symmetry to seven possible models are summarized. Models 1 and 2 require metal-metal bonds, whilst in the others there are pseudo-rings of 2, 4, 6, 8, and 10 carbon monoxide groups. All these models, with the exception of model 3 (*vide infra*) are consistent with the absence of ketonic bridging frequencies.

As an example of the method of calculation used in obtaining Table 2, we shall consider the model 4 (3-4-3). The molecule is first resolved into two groups of carbon monoxide ligands each having the symmetry C_{3v}, and one group having the symmetry D_{4h}. Using customary group theoretical methods, we find that the C_{3v} groups give *two* allowed frequencies of species A_1 and E. Similarly, the D_{4h} group has two allowed frequencies of species A_{2u} and E_u. However, for this second group, a C-O *stretching* mode of symmetry A_{2u} does not exist, and thus for the whole molecule, only *three* distinct infra-red active frequencies would be expected.

5-0-5 *models*. Four possible models have been considered. The pyramidal (5-0-5) models consist of two $M(CO)_5$ groups, each forming a pentagonal pyramid and joined at the metal atoms so as to have a common five-fold axis. Both the staggered (D_{5d}) and eclipsed (D_{5h}) configurations have been considered. In the octahedral (5-0-5) models, each metal atom is octahedrally co-ordinated by five CO groups and the other metal atom; again, staggered and eclipsed configurations are possible.

It is seen that all four (5-0-5) models may be eliminated, since only two C-O stretches would be expected in each case.

While it might be possible to construct, *ad hoc*, one, or perhaps several, (5-0-5) models giving three bands, they would be of rather peculiar symmetry. We consequently consider these highly unlikely, since the metal carbonyls appear to assume as symmetrical structures as possible, as far as can be ascertained at present.

TABLE 1. SOME OBSERVED INFRA-RED FREQUENCIES IN $Mn_2(CO)_{10}$ AND $Re_2(CO)_{10}$

Frequency, cm^{-1}		Physical state of sample	Assignment
$Mn_2(CO)_{10}$	$Re_2(CO)_{10}$		
2060 2014 1989		Solid in KI wafer	
2076 2028 1996	2067 2008 1965	Solution in $CHCl_3$	
2061 2027 1998	2065 2006 1968	Solution in CS_2	Carbonyl stretching frequencies
2063 2028 1997		Solution in CCl_4	
2068 2039 2006	2070 2019 1985	Gas	
648 642	582 574	Solution in CS_2	Metal-carbon stretching frequencies

It will be shown below that by consideration of carbon-metal stretching frequencies it is possible to eliminate conclusively all (5-0-5) models.

4-2-4 *model*. This model agrees with experiment with respect to the *number* of bands, but the concept of a pseudo-ring of only two C-O groups seems to be a contradiction in terms; thus, such a model would be expected to show ketonic stretching frequencies, and is consequently discarded.

1-8-1 *and* 0-10-0 *models*. These models include only one possibility consistent with experiment, namely the D_{4d} (1-8-1) model. The existence of such a large puckered ring seems intrinsically unlikely on chemical and intuitive grounds, and is hence discarded.

3-4-3 *and* 2-6-2 *models*. These remain the only possibilities for models consistent with the observed spectrum and not subject to any other obvious objection. We have then model 4, a (3-4-3) model with a planar four-membered ring (D_{4h}), and

Table 2. Infra-red active carbonyl frequencies for various models of $Mn_2(CO)_{10}$ and $Re_2(CO)_{10}$

Structure Number	Structural type	IR-allowed end group frequencies	IR-allowed ring frequencies	Total No. of active CO frequencies
1	(5-0-5) pyramidal, D_{5d} or D_{5h}	A_{2u}, E_{1u} for D_{5d} A_2'', E_1' for D_{5h}	—	2 for D_{5d} or D_{5h}
2	(5-0-5) octahedral	B_2, E_1 for D_{4d} A_{2u}, E_u for D_{4h}	—	2 for D_{4d} or D_{4h}
3	(4-2-4) pyramidal	A_1, E for local symmetry C_{4v}	B_{2u} for local symmetry D_{2h}	3
4	(3-4-3) pyramidal	A_1, E for local symmetry C_{3v}	E_u for symmetry D_{4h}	3
			B_2, E for symmetry D_{2d}	4
5	(2-6-2)	A_1, B_2 for local symmetry C_{2v}	E_{1u} for local symmetry D_{6h}	3
			A_{2u}, E_{2u} for local symmetry D_{3d}	4
6	(1-8-1)	Σ_u^+	E_{1u} for local symmetry D_{8h}	2
			B_2, E_1 for local symmetry D_{4d}	3
7	(0-10-0)	—	E'_1 for local symmetry D_{10h}	1
			A_{2u}, E_{1u} for local symmetry D_{5d}	2

model 5, a (2-6-2) model with a planar six-membered ring. These models are illustrated in Fig. 2. From the spectroscopic data it is not possible to decide which of these two models is the more likely.

It may be noted that in $C_5H_5Mo(CO)_6MoC_5H_5$[7] and in $C_5H_5W(CO)_6WC_5H_5$, which have very similar spectra, it was found that the pseudo-rings were necessarily puckered, whilst for $Mn_2(CO)_{10}$ and $Re_2(CO)_{10}$, only planar or nearly-planar rings[8] will fit the observed spectrum.

The Nature of the Bonding in the Pseudo-ring Carbonyl System

While it is not possible to discuss the nature of the bonding in the pseudo-ring system or the bonding between the systems and the metal atoms in great detail, a few remarks seem to be well founded and apposite.

[7] The existence of a compound $C_5H_5Mo(CO)_3MoC_5H_5$ seems to be dubious and the compound $C_5H_5Mo(CO)_6MoC_5H_5$ prepared by oxidation of $C_5H_5Mo(CO)_3H$ has the same crystal structure as the tungsten compound. [See T. S. Piper and G. Wilkinson, *Naturwiss.* **42**, 625 (1955) and F. C Wilson and D. P. Shoemaker, *Naturwiss.* (in press).]

[8] If the deviations from planarity are small, the methods of reference (1) yield a resultant spectrum similar in nature to that of the planar model. See also A. D. Liehr, *J. Chem. Phys.* (in press).

The term pseudo-ring has been used with the understanding that the bonds between the carbon atoms constituting these rings of CO ligands are believed to be weak. This statement, as well as the assumption that no individual CO group in the ring forms a definite localized bond to the metal atom, follows from the fact that the absorption in the infra-red by these CO groups occurs in or only slightly below the range for simple terminal CO groups. Thus the electron density in these ring CO ligands is not greatly different from that in the terminal CO groups. It is therefore

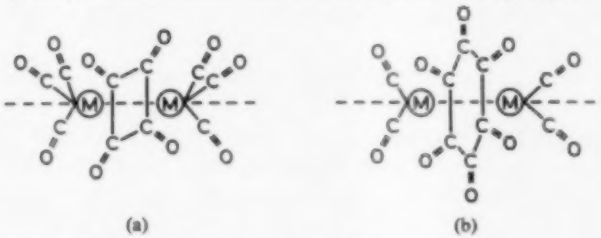

FIG. 2.—Acceptable models for $Mn_2(CO)_{10}$ and $Re_2(CO)_{10}$.
(a) The (3-4-3) model.
(b) The (2-6-2) model.

unlikely that the amount of electron density withdrawn for metal-ring bonding per CO group is very great. A further indication of this is to be found in the observation that only two absorption bands are observed in the region of carbon-metal stretching frequencies (Table 1).

For either of the structures preferred for $Mn_2(CO)_{10}$ and $Re_2(CO)_{10}$, these frequencies are most logically assigned to the *terminal* CO groups, for in each of these models the terminal groups alone require just two carbon-metal stretching frequencies. Since no strong absorption bands other than those listed in Table 1 were found, it seems reasonable to conclude that the stretching frequencies of the ring carbon-metal bonds occur below 450 cm^{-1}, and therefore that these bonds are individually rather weak. In compounds containing ketonic CO bridges, the relatively strong localized carbon-metal bonds formed by the bridging CO groups occur in the same range as the carbon-metal stretching frequencies of the terminal CO groups.[9]

It may be also noted here that the occurrence of only two carbon-metal stretching frequencies, although there are *three* carbonyl stretching frequencies, conclusively eliminates any (5-0-5) model, for in *any* (5-0-5) model, all carbon-metal bonds would form a set symmetrically equivalent to the carbon-oxygen bonds,[10] and therefore the number of carbon-metal frequencies would have to equal the number of C-O frequencies.

The diamagnetism of $Mn_2(CO)_{10}$ and $Re_2(CO)_{10}$ may be explained on the basis of pseudo-ring structures, without the assumption of metal-metal bonds or of pairing of spins on the metal atoms. It is only necessary to assume that an odd number of electrons from the ring enter the orbitals of each metal atom.

It is in fact possible to consider the primary metal to pseudo-ring bonding here as an example of the delocalized type of bond exemplified by the metal to cyclopentadienyl-ring bonds in the π-cyclopentadienyl compounds of transitional metals.[11]

[9] This statement is based upon unpublished work by the authors on $Fe_3(CO)_9$, $Fe_2(CO)_{12}$, and $Co_2(CO)_8$.
[10] This statement depends upon the fact that M-C-O grouping (for end-groups) is linear.
[11] MOFFITT, W., *J. Amer. Chem. Soc.* **76**, 3386 (1954).

With this type of bonding, a cup-shaped orbital of the metal atom overlaps orbitals of suitable symmetry in a ring of carbon atoms. On such a basis the (1-8-1) model would be virtually excluded, since such a ring would be too large to permit effective overlap with the metal orbital. The latter has a size suitable for good overlap with a five-membered ring, and probably with four- or six-membered rings also.

Acknowledgements—We are indebted to the General Electric Company for a Swope fellowship (F. A. C.) and to the National Science Foundation for a pre-doctoral fellowship (A. D. L.).

This work was supported in part by the Atomic Energy Commission.

Errata in reference (1): In eq. (2) and (5), which are kinetic energy expressions, the reduced mass μ appears in the denominator, whereas it should of course be in the numerator. This error does not affect any of the end results, which were only intensity *ratios*.

J. Inorganic and Nuclear Chemistry, 1956, Vol. 2, pp. 149–152. Pergamon Press Ltd., London

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DI(π-CYCLOPENTADIENYL)TITANIUM(II)*

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(*Received* 14 *September* 1955)

Abstract—*Di*(π-cyclopentadienyl)titanium(II) has been prepared by the reaction of titanium dichloride with sodium cyclopentadienide in tetrahydrofuran solution. The compound forms dark green crystals; it is exceedingly reactive with air, and decomposes thermally below its melting-point.

A tetrahydrofuran etherate of *di*(π-cyclopentadienyl)titanium is also described; this compound exists in two forms, a green paramagnetic form which transforms spontaneously into a brown diamagnetic form.

1. INTRODUCTION

IN a previous paper,[1] the preparation and properties of *di*(π-cyclopentadienyl) dihalides of titanium(IV), such as $(C_5H_5)_2TiCl_2$, have been described; it was also shown that aqueous solutions of the halides could be reduced to give the *di*(π-cyclopentadienyl)titanium(III) ion $[(C_5H_5)_2Ti]^+$. The neutral compound, *di*(π-cyclopentadienyl)titanium(II) has now been prepared by the reaction of titanium dichloride with sodium cyclopentadienide in tetrahydrofuran solution. The neutral compounds, $(C_5H_5)_2M$, of all the elements of the first transitional series have now been prepared; previous papers have described the compounds of vanadium,[2] chromium,[3, 4] manganese,[5, 6, 7] iron,[8, 9] cobalt,[10, 11] and nickel.[10, 12]

2. THE NATURE OF *DI* (π-CYCLOPENTADIENYL)TITANIUM(II)

With the exception of manganese cyclopentadienide, $(C_5H_5)_2Mn$, in which the metal-to-ring bonds have been shown to be electrostatic in nature,[6, 13] the $(C_5H_5)_2M$ compounds of V, Cr, Fe, Co, and Ni appear to have metal-to-ring bonds of the "sandwich bond" or π-cyclopentadienyl type; this is shown, for example, by the similarity of the mass patterns in mass spectrometric studies.[13] However, in solvents of high dielectric constant and in some chemical reactions, $(C_5H_5)_2V$ and $(C_5H_5)_2Cr$ show unusual behaviour.[6] In liquid ammonia and in tetrahydrofuran, solvates are

* We adopt the nomenclature (π-cyclopentadienyl) for "sandwich bonded"[14, 15] cyclopentadienyl groups.

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[13] L. FRIEDMAN, A. P. IRSA, and G. WILKINSON, *J. Amer. Chem. Soc.* **77**, 3689 (1955).
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formed, and also these compounds react with ferrous chloride in tetrahydrofuran to form ferrocene, although not quantitatively as does $(C_5H_5)_2Mn$, in addition to being oxidized. *Di*(π-cyclopentadienyl)titanium does not resemble $(C_5H_5)_2V$ and $(C_5H_5)_2Cr$ in these respects however, and the chemical evidence indicates that the metal-to-ring bonds are homopolar bonds of the "sandwich bond" type, and that they are unaffected by the fields due to dipolar solvent molecules surrounding the metal atom in the exposed region between the cyclopentadienyl rings. Thus $(C_5H_5)_2Ti$ does not form a solvate with liquid ammonia, and gives essentially non-electrolytic solutions in this solvent. With ferrous chloride in tetrahydrofuran solution, a very sensitive test of ionic dissociation of a $(C_5H_5)_2M$ compound, $(C_5H_5)_2Ti$ does not produce ferrocene, even in the trace amounts that are formed in the reaction of $(C_5H_5)_2V$ with ferrous chloride.

The magnetic properties of $(C_5H_5)_2Ti$ are of considerable interest. According to the molecular orbital treatment[14] of the metal-to-ring bonding in neutral *di*-π-cyclopentadienyl compounds of the metals of the first transitional series, a diamagnetic molecule $(C_5H_5)_2Ti$ may be expected. Owing to the difficulty of assessing quantitatively the position of balance between orbital and Hund stabilization, no definite prediction was possible, and this was true also for $(C_5H_5)_2V$.

On the other hand, according to DUNITZ and ORGEL,[15] a triplet state for $(C_5H_5)_2Ti$ is anticipated. *Di*(π-cyclopentadienyl)titanium is *diamagnetic* in the solid state and also in solution in petroleum ether and in tetrahydrofuran. If the metal-to-ring bonds were heteropolar in nature, or if they were not of the "sandwich bond" type, but were localized bonds between the metal atom and a carbon atom of the C_5H_5 ring, it is unlikely that the molecule would be diamagnetic. The diamagnetism of $(C_5H_5)_2Ti$ thus is not only in accordance with MOFFITT's views, but provides further evidence for the homopolar nature of the metal-to-ring bond.

That the lower *s-d* hybrid orbital (ha_g) postulated by MOFFITT, which allows of the possibility of diamagnetism for $(C_5H_5)_2Ti$, is at a level not too far below those of the remaining unfilled 3*d* orbitals, is suggested by the fact that the perturbing field due to the solvent molecule in the crystalline etherate $(C_5H_5)_2Ti \cdot C_4H_8O$, allows of the existence of two forms of this compound. A paramagnetic green form is obtained by cooling the green melt or by sublimation, but it converts spontaneously to a diamagnetic brown form.

In unsolvated $(C_5H_5)_2Ti$, however, it is possible to say that the excited triplet state must lie at a level greater than kT above the ground singlet state, since the susceptibility of the compound does not vary from 77° to 380°K.

3. EXPERIMENTAL

Materials

We are greatly indebted to the National Lead Company (Titanox Division), South Amboy, New Jersey, the New Jersey Zinc Company, Palmerston, New Jersey, and the Linde Air Products Company, Tonawanda, New York, for various gifts of titanium dichlorides and trichlorides. We have also prepared titanium dichloride by passing hydrogen chloride over titanium hydride (Metal Hydrides, Inc., Beverley, Mass.) for two hours at 650°C; the product was finely ground and was then heated in vacuum at 550°C for 4–5 h to disproportionate the trichloride formed together with dichloride in the reaction. This product analysed ~65 per cent titanium dichloride.

Tetrahydrofuran was purified by distillation in nitrogen from lithium aluminium hydride.

All operations with titanium dichloride and with *di*(π-cyclopentadienyl)titanium were carried out in an inert atmosphere, using a gloved box which could be pumped out and subsequently filled with argon. A stream of purified nitrogen was passed through the reaction vessels during the preparations.

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Preparation of di(π-cyclopentadienyl)*titanium*

Sodium (5·9 g, 0·256 mol) was dispersed in boiling toluene, and, after cooling, the solvent was replaced by tetrahydrofuran (150 ml). Cyclopentadiene (22 ml, 0·256 mol) was added slowly with stirring and ice-cooling. After evolution of hydrogen ceased, titanium dichloride (10 g, 0·12 mol) was added to the pale orange solution of sodium cyclopentadienide. The reaction mixture, which rapidly became green, was stirred at 25°C for 2–3 h. The solvent was then removed in vacuum, and the dry residue transferred to the thimble of an extraction apparatus designed for operation in an inert atmosphere.[16] The residue was extracted with petroleum ether (30–60°) or with ligroin (90 –120°) which had been washed with concentrated sulphuric acid and with water and subsequently dried. The green petroleum solution was evaporated and the solid transferred to a suitable sublimation apparatus. At 120–180°C at 10^{-3} mm Hg *di*(π-cyclopentadienyl)titanium sublimed and collected on a cooling probe as dark green crystals. Yield ~5·5 g (~40 per cent based on $TiCl_2$). The cooling probe must be placed close to the surface of the crude product in order to minimize thermal decomposition of $(C_5H_5)_2Ti$ in the vapour phase; some decomposition seems to be unavoidable, however, and if the compound is sublimed repeatedly down a tube, even at temperatures as low as 100°C, a residue is always left behind.

Analysis of the compound is difficult, due to the extreme reactivity with even traces of oxygen. We are indebted to Dr. E. O. BRIMM of Linde Air Products, Tonawanda, New York, for arranging to have carbon and hydrogen analyses carried out for us. The titanium was determined by weighing TiO_2. (*Anal.* Required for $(C_5H_5)_2Ti$; C 67·45, H 5·65, Ti 26·90. Found: C 63·0, H 5·2, Ti 26·1.)

Properties of di(π-cyclopentadienyl)*titanium*

In a sealed evacuated tube, substantial decomposition of the compound begins at temperatures above ~130°, and a melting-point cannot be observed. The compound is sensitive towards air and is completely oxidized and destroyed on exposure. It is stable in light and in vacuum or an inert atmosphere in the solid state or in solution.

The compound is readily soluble in petroleum, benzene, and other hydrocarbon solvents, and in ethers; the solutions are green. It reacts instantaneously with carbon disulphide. With carbon tetrachloride a red solution is formed which rapidly deposits a black solid; the compound is completely destroyed. With maleic anhydride in benzene solution, a dark-coloured solid is formed immediately. There is no reaction with carbon dioxide. The compound is insoluble in, and reacts only very slowly over a period of several hours with, air-free water. With dilute hydrochloric or sulphuric acids, it is oxidized to yellow solutions of the *di*(π-cyclopentadienyl)-hydroxytitanium(IV) cation. These were characterized by their formation of precipitates with silicotungstic acid and REINECKE's salt. From concentrated hydrochloric acid solutions, $(C_5H_5)_2TiCl_2$ was isolated by evaporation and solvent extraction. These oxidation reactions of $(C_5H_5)_2Ti$ confirm the "sandwich" nature of the molecule.

Di(π-cyclopentadienyl)titanium is only slightly soluble in liquid ammonia, and gives a pale green solution. The solution conducts electricity only slightly more than the solvent itself, and this small conductivity may be due to traces of impurities such as $(C_5H_5)_2TiCl_2$. There is no evidence for the formation of solvates as occurs with $(C_5H_5)_2V$ and $(C_5H_5)_2Cr$.[6]

Reaction with Ferrous Chloride

Di(π-cyclopentadienyl)titanium was allowed to react in tetrahydrofuran solution with ferrous chloride; the latter was prepared in a highly reactive form by reduction of ferric chloride with iron powder in tetrahydrofuran.[6] The compound is at once oxidized to the cation $[(C_5H_5)_2Ti]^+$, which in tetrahydrofuran is indigo in colour.[17] This ion can be further oxidized by the addition of aqueous acids together with a little dilute nitric acid to the yellow $[(C_5H_5)_2TiOH]^+$ ion.

No trace of ferrocene was detected when the ferrous chloride reaction mixtures were worked up for this compound.

[16] W. F. BARTHEL, *Ind. Eng. Chem.* (Anal Edition) **17**, 53 (1945).

[17] As with the hydrated Ti^{3+} ion, which exists in green and violet forms, the $[(C_5H_5)_2Ti]^+$ ion also has two forms. In the reduction of $[(C_5H_5)_2TiOH]^+$ in a Jones reductor, the purple solution initially formed in the column changes very rapidly to green, and the eluate is green. Reduction of $(C_5H_5)_2TiCl_2$ in non-aqueous media, e.g., by zinc, also gives green solutions.

Magnetic Measurements

Approximately 0·1M solutions of $(C_5H_5)_2Ti$ in petroleum ether and in tetrahydrofuran were prepared in a vacuum apparatus and were passed through a sintered glass filter into a Gouy tube, which was then sealed off. Measurements of the solutions and of the pure solvents showed that $(C_5H_5)_2Ti$ was diamagnetic. Measurements were also made on the solid, using previously-described techniques;[6] at 25°C, χ mol $= -100 \pm 10 \times 10^{-6}$ c.g.s.u. No change in the susceptibility of the solid could be detected at liquid-nitrogen temperature and at 100°C; measurements at higher temperatures were not made, in view of the possibility of thermal decomposition of the compound.

The susceptibility of $(C_5H_5)_2V$, which was measured at 90°K and 293°K and was found to obey CURIE's law,[2] was checked over a wider temperature range, and the observation that $(C_5H_5)_2V$ has three unpaired electrons confirmed. The values for the molar susceptibility ($\times 10^6$ c.g.s.u.) corrected for diamagnetism (-90×10^{-6} c.g.s.u.) of the rings are: 78°K, + 22, 100; 195°K, + 9150; 273°K, + 6600; 306°K, + 5840; 370·5°K, + 4920; 391°K, + 4640; 428°K, + 4130. Over this range, $\mu_{eff} = 3{\cdot}82$ B.M. The susceptibility measured in dilute solution (0·012 g/ml) in petroleum at 25°C led to the same value for μ_{eff}.

The di(π-*cyclopentadienyl*)*titanium-tetrahydrofuran Etherate*

Before the procedure for the preparation of $(C_5H_5)_2Ti$ noted above was developed, attempts were made to sublime the compound directly from the crude evaporated sodium-cyclopentadienide reaction mixture. In two cases, about 100 mg of a compound which sublimed from the mixture at ~80°C was obtained. This proved to be an etherate.

[*Analysis*: Found, C 63·0, H 7·5, Ti 19·3; required for $(C_5H_5)_2TiC_4H_8O$; C 67·2, H 7·2, Ti 19·2.] The compound condenses from the vapour as green crystals. The composition was confirmed by thermal decomposition at 150°C in vacuum; *di*(π-cyclopentadienyl)titanium, characterized by acid oxidation, and tetrahydrofuran, characterized by its infra-red absorption spectrum, were obtained.

Under the polarizing microscope, the green crystals of the etherate appear to be monoclinic. When the crystals are allowed to stand, a spontaneous transformation occurs: the green crystals break up, and brown crystals, suggested by microscopic examination to be tetragonal, are formed. At 25°C the transformation is complete in about 30 min, and at 0°C in a few hours; the green form can be stabilized by rapid chilling to −80°C, but when temperature rises, the change to the brown form begins.

The brown form of the compound is quite stable up to its melting-point at 81 ± 0·5°C: then a green melt is formed, which crystallizes as the green form of the compound. These changes are completely reversible without decomposition.

Although the solid has not been isolated in quantities sufficient to allow precise determinations of the susceptibilities with the apparatus available to us here, magnetic measurements show conclusively that the brown form is diamagnetic and the green form is paramagnetic.

The chemical reactivity of the etherate is similar to that of $(C_5H_5)_2Ti$.

Acknowledgements—We are indebted to Dr. J. M. BIRMINGHAM for his assistance in part of the experimental work and to Professor W. MOFFITT for helpful discussion.

This work was supported in part by the Atomic Energy Commission.

J. Inorganic and Nuclear Chemistry, 1956, Vol. 2, pp. 153–163. Pergamon Press Ltd., London

THE TRINITRATOURANYL ION IN ORGANIC SOLVENTS[1]

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(*Received* 22 *September* 1955)

Abstract—The enhanced extraction of uranyl nitrate into ketonic solvents in the presence of a substituted ammonium nitrate RNO_3 has been shown to be caused by the formation of a complex $RUO_2(NO_3)_3$. The formula of the complex has been deduced from solvent extraction and spectrophotometric studies, and the anionic nature of the uranium has been demonstrated by electrolytic transference measurements. Factors affecting the stability of the complex include the nature of the solvent, its water content, and the structure of the cation *R*.

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IN the course of work at this laboratory on the purification of uranyl nitrate by extraction from aqueous nitric acid into methyl isobutyl ketone, it was observed that the extractability was greatly increased when hydrazine was present in the system. It was established that, in the ketonic solvent, hydrazine is converted to the ketazine $\left[(CH_3)_2CHCH_2C(CH_3)=N-\right]_2$ which is present as its nitrate salt. It was further shown that other nitrate salts sufficiently soluble in the organic solvent cause a similar enhancement of uranium extraction. In this paper it is demonstrated that, in the presence of these nitrate salts, uranium is extracted into the organic phase as a trinitratouranyl complex $RUO_2(NO_3)_3$, in which the uranium is present as an anion. A spectrophotometric study of the trinitratouranyl ion and of some of the factors affecting its stability are also presented. (Since the completion of this work evidence has been reported for the formation of the tetramethylammonium trinitratouranyl complex in anhydrous nitric acid[2] and of the corresponding diethylammonium compound in dinitrogen tetroxide.[3]

Effect of Organic Nitrates on the Extractability of Uranyl Nitrate

Uranyl nitrate is extracted from aqueous solution by methyl isobutyl ketone to an extent which varies with the concentration of nitric acid and the nature and concentration of an inorganic nitrate used as a salting-out agent. It was found that the addition of relatively small amounts of an organic-soluble nitrate to the system markedly increased the concentration of uranium in the organic phase. In Table 1 are summarized the results of a number of experiments carried out, using equal volumes of methyl isobutyl ketone and of an aqueous solution 8*M* in ammonium nitrate, 0·4*M* in nitric acid, and about 0·02*M* in uranyl nitrate. Varying concentrations (small compared to that of inorganic nitrate) of several different substituted ammonium nitrates were added to the mixtures, the systems were equilibrated, and

[1] This paper is based on Argonne National Laboratory reports ANL-4520 and ANL-4521, declassified 6 December 1950. Work performed under the auspices of the U.S. Atomic Energy Commission.
[2] G. JANDER and H. WENDT, *Z. anorg. Chem.* **258**, 1 (1949).
[3] C. C. ADDISON and N. HODGE, *Nature* **171**, 569 (1953).

TABLE 1.—EFFECT OF SUBSTITUTED AMMONIUM NITRATES (RNO_3) ON THE EXTRACTION OF URANYL NITRATE BY METHYL ISOBUTYL KETONE[a]

Cation R	$[RNO_3]_{tot}$ mol/l. $\times 10^2$	$[U]_{aq}$ mol/l. $\times 10^2$	$[U]_{org}$ mol/l. $\times 10^2$	Q[f]	K'[g]
None	0	5·8	15·2	2·62	
$(C_4H_9)_2NH$	2·1	5·90	18·0	6·2	130
	4·2	1·80	19·2	10·7	110
	11·0	0·60	19·4	32·4	120
	21·0	0·29	19·6	68	130
$(C_8H_{17})_2NH_2$[b]	2·5	3·0	18·0	6·0	88
	5·0	2·0	18·8	9·4	73
	10·0	1·2	19·8	16·5	65
	20·0	0·60	19·8	33	65
$C_{11}H_{15}NH$[c]	2·0	3·3	17·8	5·4	100
	5·0	1·4	18·8	13·4	120
	10·0	0·75	20·0	26·7	110
	20·0	0·34	19·3	57	110
$C_{12}H_{24}N_2H$[d]	2·1	2·90	15·9	5·5	86
	10·5	0·73	18·7	25·6	100
$(C_4H_9)_4N$	10·0	0·20	19·4	97	440
	10·0	0·23	19·3	84	380
C_6H_7NH[e]	10·0			2·8	0·8
$(C_3H_6)_3NH$	10·0			4·0	5·4
$(CH_2CH_2OH)_4N$	10·0			2·67	0·2

[a] Aqueous phase: $8M$ NH_4NO_3, $0{\cdot}4M$ HNO_3. [b] di-2-ethylhexylammonium. [c] 2-*n*-hexylpyridinium. [d] methyl isobutyl ketazinium. [e] 2-methylpyridinium.
[f] $Q = [U]_{org}/[U]_{aq}$. [g] $K' = \frac{Q - Q_0}{Q_0} \cdot \frac{1}{[RNO_3]_{tot} - [RUO_2(NO_3)_3]}$.

the concentration of uranium in each phase was determined. In each case, the distribution coefficient Q (organic/aqueous) is greater than in the absence of the organic nitrate, the value of Q increasing with increasing concentration of the latter.

Since the distribution coefficient for uranium in this system is not sensitive to changes in the ammonium nitrate concentration comparable to the amount of added organic nitrate, or to changes in the uranyl nitrate concentration below $0{\cdot}02M$, it is concluded that the effect of the organic nitrate must be caused by the formation of a uranium complex in the organic phase. That the complexing agent is nitrate ion, rather than the amine moieties of the salts, is indicated by the fact that the quaternary ammonium salt, tetrabutylammonium nitrate, is even more effective than the salts of the secondary and tertiary amines.

The number of molecules of the substituted ammonium nitrate RNO_3, per molecule of uranyl nitrate in the complex, was estimated from the dependence of the distribution coefficient on the concentration of the complexing agent. For a one-to-one complex, $RUO_2(NO_3)_3$, the association constant is given by

$$K = [RUO_2(NO_3)_3]/[UO_2(NO_3)_2]\,[RNO_3]. \quad (1)$$

If the complexing agent has no effect on the equilibria existing in the aqueous phase, as seems probable, the concentration of uncomplexed $UO_2(NO_3)_2$ in the organic phase in each system is the product of the concentration of uranium in the aqueous phase by the distribution coefficient Q_0 in the absence of complexing agent. The concentration of $RUO_2(NO_3)_3$ is then the difference between the total uranium in the organic phase and the $UO_2(NO_3)_2$ thus calculated. The concentration of RNO_3 in the organic phase is the difference between the total RNO_3 in that phase and the amount tied up in the complex. If all of the RNO_3 remained in the organic phase, the association constant K would be related to the distribution coefficient Q by the expression

$$K = \frac{Q - Q_0}{Q_0} \cdot \frac{1}{[RNO_3]_{tot} - [RUO_2(NO_3)_3]}. \quad (2)$$

Since some of the RNO_3 distributes into the aqueous phase, this expression gives, not the association constant K, but a related constant,

$$K' = K \cdot \frac{[RNO_3]_{org}/(RNO_3)_{aq}}{1 + [RNO_3]_{org}/[RNO_3]_{aq}}. \quad (3)$$

In Table 1, values of K' calculated by means of equation (2) are listed. The constancy of these values for a given salt RNO_3 over a fairly wide range of concentration is evidence for the formation of a one-to-one complex. Similar calculations assuming other ratios of RNO_3 to $UO_2(NO_3)_2$ in the complex lead to no such constancy.

The variations in K' with the nature of the cation R is attributable in part, as indicated in equation (3), to differences in the distribution of the salt RNO_3 between the two phases. In particular, the low values of K' observed for the last three compounds in Table 1 are associated with the highly preferential solubility of these compounds in the aqueous phase. The higher value of K' observed with tetrabutylammonium nitrate than with the first four compounds listed is probably related, at least in part, to differences in the true association constants K, as will be discussed below in connection with the spectrophotometric measurements.

Electrolytic Transference Experiments

The sign of the charge on the uranyl complex in solutions of substituted ammonium nitrates in methyl isobutyl ketone was established by determining the direction of migration in an electric field. Both in 0·1*M* triethylammonium nitrate and in 0·05*M* tetrabutylammonium nitrate the uranium was found to migrate almost quantitatively toward the anode. The uranyl group must, therefore, be present in these solutions as an anionic complex $[UO_2(NO_3)_{2+z}]^{-z}$; because of the low dielectric constant of the medium, this anion is undoubtedly associated to a considerable extent with the substituted ammonium cation as ion pairs.

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The behaviour of the uranium in these solutions is quite in contrast with that in aqueous solution: In 1*M* aqueous nitric acid the uranium migrates quantitatively towards the cathode.

Spectrophotometric Studies

The absorption spectra of solutions of uranyl nitrate in methyl isobutyl ketone, in acetone, and in cyclohexanone are shown in Fig. 1. These spectra are quite similar to one another, each consisting of a broad absorption band centring at about 426 mμ, upon which are superimposed a number of well-defined maxima. They differ from the spectrum of uranyl nitrate in water (Fig. 2) most markedly in the sharpness of the bands at about 426, 440, 455, and 470 mμ. The addition of a soluble nitrate salt to a solution of uranyl nitrate in one of the ketones produces a striking change in the spectrum, the major effect being to increase the intensity of the four maxima mentioned above, with relatively little change in their wavelengths or in the absorption at the adjacent minima. The spectrum of an equimolar mixture of uranyl nitrate and tetrabutylammonium nitrate in acetone is included in Fig. 1. The spectrum is not further changed by addition of excess tetrabutylammonium nitrate, and is essentially the same as that produced by the addition of a number of other nitrates to uranyl nitrate solutions in methyl isobutyl ketone or cyclohexanone. The position and intensity of three of the maxima in several such solutions are recorded in Table 2.

The linearity of the increase in intensity with the concentration of added nitrate salt up to the concentration of uranyl nitrate, with no further increase beyond this point, is in accord with the formation of a complex $RUO_2(NO_3)_3$, of considerable stability. That this is indeed the correct formulation was borne out by application of

TABLE 2.—EFFECT OF NITRATE SALTS, RNO_3, ON THE ABSORPTION SPECTRUM OF URANYL NITRATE IN KETONE SOLUTIONS[a]

Solvent	Cation *R*	(RNO_3) mol/l.	λ_{max} mμ	E_{max}	λ_{max} mμ	E_{max}	λ_{max} mμ	E_{max}
Acetone			471	4·1	455	7·0	440	10·0
	Bu_4N	0·01	470	12·0	455	18·9	441	18·2
	Bu_4N	0·02	470	19·8	455	30·5	441	26·6
	Bu_4N	0·04	470	19·8	455	30·6	441	27·5
M.I.B.K.[b]			470	3·6	454	6·0	440	10·2
	Bu_4N	0·01	471	12·7	456	19·9	441	20·2
	Bu_4N	0·02	471	20·8	456	31·8	441	29·2
	Bu_4N	0·04	471	19·8	456	31·0	442	26·5
	Bu_3NH	0·04	472	19·8	456	31·0	442	26·5
	C_5H_5NH[c]	0·04	471	20·4	456	30·8	441	27·3
	$C_{13}H_{24}N_2H$[d]	0·04	471	19·8	456	30·0	441	27·0
Cyclohexanone			471	4·2	455	6·4	441	9·6
	Et_2NH	0·02	471	16·8	456	27·0	441	22·5
		0·04	471	18·3	456	29·7	441	25·0

[a] $UO_2(NO_3)_2 \cdot 6H_2O = 0{\cdot}02M$. [b] methyl isobutyl ketone. [c] pyridinium. [d] methyl isobutyl ketazinium.

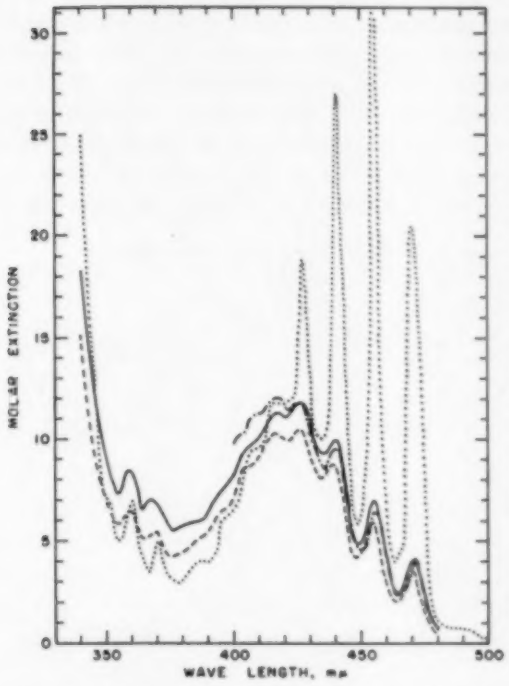

FIG. 1.—Absorption spectra of uranyl nitrate in ketonic solvents. 0·02*M* $UO_2(NO_3)_2 \cdot 6H_2O$: —— in acetone; - - - - in methyl isobutyl ketone; ——— in cyclohexanone; ····· in acetone, 0·02*M* Bu_4NNO_3.

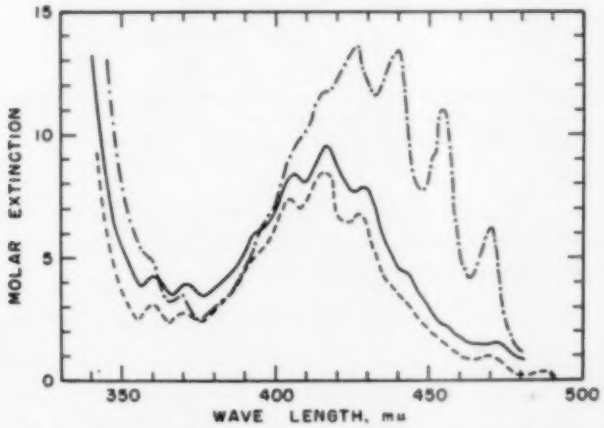

FIG. 2.—Absorption spectra of uranyl nitrate in some aqueous solutions. —— 0·02*M* in H_2O; – – – 0·00974*M* in 0·514*M* HNO_3 (from R. E. CONNICK *et al.*, Ref. 13, p. 590); ——— 0·02*M* in 16*M* HNO_3.

the method of continuous variations[4] to solutions of uranyl nitrate and tetrabutylammonium nitrate in methyl isobutyl ketone. In Fig. 3 is plotted the increase in optical density Y above that expected in the absence of interaction between the reagents, against the ratio X of the volume of 0·05M uranyl nitrate to the sum of the volumes of 0·05M uranyl nitrate and 0·05M tetrabutylammonium nitrate. For each of the two wavelengths studied, 455 and 470 mμ, the points fall very close to straight lines intersecting at a ratio X of 0·50, corresponding to an equimolar mixture of the two reagents. There is no discontinuity at a point corresponding to two moles of

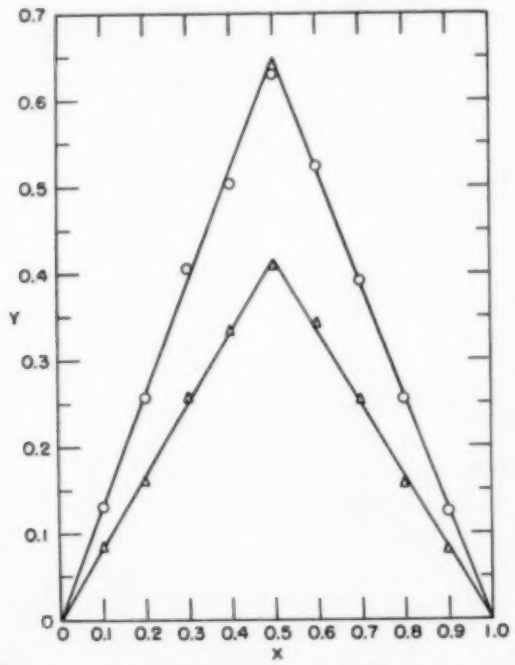

FIG. 3.—Spectral interaction between uranyl nitrate and tetrabutylammonium nitrate in methyl isobutyl ketone.
○ 455 mμ, △ 470 mμ. 0·05M solutions. X = volume uranyl nitrate solution/total volume; Y = excess optical density.

tetrabutylammonium nitrate per mole of uranyl nitrate. The absence of curvature in the plots bespeaks a high degree of stability for the trinitratouranyl complex: an association constant of about 10^5 for the reaction

$$UO_2(NO_3)_2 + Bu_4NNO_3 \rightleftharpoons Bu_4NUO_2(NO_3)_3$$

is indicated by the difference between the optical densities observed for the equimolar mixture and those corresponding to the intersections of the straight lines.

Factors Affecting the Stability of the Trinitratouranyl Complex

The association constant for the reaction between uranyl nitrate and tetrabutylammonium nitrate in acetone, like that in methyl isobutyl ketone, is about 10^5. The

[4] W. C. VOSBURGH and G. R. COOPER, *J. Amer. Chem. Soc.* **63**, 437, (1941).

association with tetrapropylammonium nitrate is equally strong. With the nitrate salts of secondary and tertiary amines, however, the association appears to be somewhat weaker. With 2-hexylpyridinium nitrate, for example, the optical density of a solution 0·02*M* each in the salt and in uranyl nitrate, corresponds to only 88 per cent complex formation, indicating a complex constant of about 3×10^3. Doubling the concentration of the salt leads to essentially complete complex formation. The incomplete complex formation cannot be attributed to the acid-base dissociation

$$C_{11}H_{18}NNO_3 \rightleftharpoons C_{11}H_{17}N + HNO_3,$$

since the addition of nitric acid has no effect on the optical absorption. The difference in stability between the complexes involving the quaternary ammonium nitrates and those of the less highly substituted ammonium salts is probably related to the greater tendency for ion-pair formation with the latter, which has been ascribed to hydrogen bonding.[5] Such ion-pair formation, which would be more pronounced with the smaller nitrate ion than with the larger trinitratouranyl ion, would tend to diminish the extent of formation of the trinitratouranyl complex.

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A similar explanation is probably applicable to the relative ineffectiveness of nitric acid with respect to formation of the trinitratouranyl complex. In methyl isobutyl ketone, the addition of concentrated nitric acid to a 0·02*M* solution of uranyl nitrate causes a change in absorption of the same character as that produced by tetrabutylammonium nitrate, but even at a concentration of 1·56*M* nitric acid only about 63 per cent of the uranium is in the form of the trinitrate. Over the range of concentration 0·046*M* to 1·56*M* nitric acid, the apparent association constant is close to unity. That the ineffectiveness of nitric acid as a complexing agent is not due solely to its effect on the properties of the medium is demonstrated by the further increase in absorption produced by adding small amounts of tetrabutylammonium nitrate to the nitric acid solutions. The results are readily explicable on the plausible assumption that the trinitratouranyl ion has a weaker affinity for the hydrogen ion than has the nitrate ion.

The spectrophotometric measurements so far discussed (except for those in nitric acid solution) were carried out in essentially dry solvent, the only water being that from the added uranyl nitrate hexahydrate. The addition of water to these solutions diminishes markedly the extent of complex formation, as shown in Table 3. The effect of water cannot be attributed solely to the increased dielectric constant of the solvent: the dielectric constant of a 20 per cent solution of water in acetone,[6] in which no evidence of trinitrate formation is observed, is 29·6; that of nitroethane, in which the complex is quite stable (see below), is 30. More probably, the effect of water on the stability of the complex is caused by competition between water and nitrate ion for a position in the co-ordination sphere of the uranyl ion. The diminution of complex formation in the presence of water must be responsible for the association constant with tetrabutylammonium nitrate deduced from the solvent extraction experiments (about 400) being lower than that found spectrophotometrically in the dry solvent (about 10^5).

[5] (*a*) E. G. Taylor and C. A. Kraus, *ibid.* **69**, 1731 (1947); (*b*) W. E. Thompson and C. A. Kraus, *ibid.* **69**, 1016 (1947); (*c*) L. M. Tucker and C. A. Kraus, *ibid.* **69**, 454 (1947).

[6] H. S. Harned and B. B. Owen, *The Physical Chemistry of Electrolytic Solutions*, Reinhold, New York, 1943, p. 118.

TABLE 3.—EFFECT OF WATER ON TRINITRATOURANYL FORMATION IN ACETONE[a]

Bu_4NNO_3 mol/l.	H_2O per cent	D_{470}	α	D_{455}	α
0	0	0·081	0	0·140	0
0·020	0	0·395	1·00	0·610	1·00
0·020	10	0·126	0·14	0·216	0·16
0·020	20	0·075	0	0·140	0

[a] $[UO_2(NO_3)_2 \cdot 6H_2O] = 0{\cdot}02M$; $D\lambda$ = optical density; $\alpha = [UO_2(NO_3)_3^-]/[U]_{tot}$.

Trinitrate Formation in Other Solvents

Solutions of uranyl nitrate in water and dilute nitric acid (Fig. 2) show no spectroscopic evidence of the presence of $UO_2(NO_3)_3^-$ ions. Only in quite concentrated nitric acid solutions do there appear the absorption bands characteristic of this complex. Even in 16*M* nitric acid, however (Fig. 3), trinitrate formation is far from complete (if it is assumed that the spectrum of $UO_2(NO_3)_3^-$ in this medium is similar to that in organic solvents) and the uranium probably exists largely as the dinitrate $UO_2(NO_3)_2$.

In alcoholic solvents, also, the trinitrate complex is much weaker than in the ketones. The addition of 0·04*M* tetrabutylammonium nitrate to a 0·02*M* solution of uranyl nitrate in either ethanol or 1-propanol produces no spectral evidence of trinitratouranyl ion formation. Complex formation is more pronounced in dioxane, but, in the presence of 0·08*M* 2-*n*-hexylpyridinium nitrate, is only about 40 per cent complete. Ethyl acetate is a somewhat more effective solvent for trinitrate complex formation, about 65 per cent of the uranium being complexed in a solution 0·02*M* each in uranyl nitrate and triethylammonium nitrate. In nitroethane, complexing is about as complete as in the ketonic solvents. The order of the solvents with respect to stability of the trinitrate complex, namely ketone > ether > alcohol > water, is essentially the inverse of the order of the stability of the solvates of uranyl nitrate, as deduced from phase studies,[7] and suggests a competition between nitrate ion and solvent molecule for a co-ordination position around the uranyl ion. The relative stabilities in ethyl acetate and in nitroethane also appear to be consistent with such a postulate. The dielectric constant of the medium would not be expected to affect very greatly the equilibrium

$$UO_2(NO_3)_2 + NO_3^- \rightleftharpoons UO_2(NO_3)_3^- ;$$

however, it would affect the ionization of the $UO_2(NO_3)_2$, and hence the overall equilibrium between uranyl ions and nitrate ions.

The Ionization of Uranyl Nitrate in Acetone

In acetone, which has a dielectric constant of 20·5 at 25°, strong electrolytes may be quite appreciably ionized. Tetrabutylammonium nitrate, for example, has an ionic

[7] L. I. KATZIN and J. C. SULLIVÁN, *J. Phys. Colloid. Chem.* **55**, 346 (1951).

dissociation constant[8] of $5{\cdot}46 \times 10^{-3}$, corresponding to about 40 per cent ionization in 0·02*M* solution. It is of interest to consider the extent of ionization of uranyl nitrate in this solvent. Nitrate ions formed by such ionization would tend to interact with undissociated $UO_2(NO_3)_2$ to give $UO_2(NO_3)_3^-$. The maximum concentration of the complex ion can be estimated, by comparison of the peak height in the absorption spectra of uranyl nitrate and of $UO_2(NO_3)_3^-$ in Fig. 1, to be less than 0·002*M* in the 0·02*M* uranyl nitrate solution. (The peaks in the uranyl nitrate spectrum are more probably those of undissociated $UO_2(NO_3)_2$; the concentration of $UO_2(NO_3)_3^-$ is then much lower than that calculated.) If the association constant for the complex is

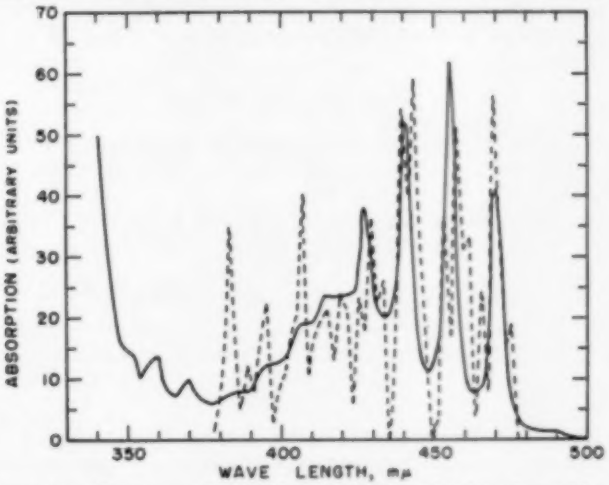

FIG. 4.—Comparison of spectrum of $UO_2(NO_3)_3^-$ in solution with that of crystalline $CsUO_2(NO_3)_3$. —— 0·02*M* $UO_2(NO_3)_2$ + 0·02*M* Bu_4NNO_3 in acetone; ---- $CsUO_2(NO_3)_3$ crystal (see text).

taken to be 10^5, as indicated by the spectrophotometric measurements previously described, the maximum value of the first ionic dissociation constant of uranyl nitrate in acetone is about 10^{-7}.

Comparison with the Spectrum of $CsUO_2(NO_3)_3$

The absorption spectra of uranyl salts, whether crystalline or in solution, are characterized by a series of absorption bands regularly spaced about 710 cm^{-1} apart.[9] Among the spectra which have been observed in solution, that of the trinitratouranyl ion appears to be unique with respect to the sharpness of its absorption bands. It is of interest to compare the spectrum of this complex with that of crystalline cesium uranyl nitrate ($CsUO_2(NO_3)_3$) which has been measured[10] at 20°K. The spectrum of this crystal, as is generally true of uranyl salts at low temperature, consists of a large number of very fine lines. As the temperature is raised, these lines broaden and blend into a continuum. If one sums the intensities of the lines in the low-temperature cesium uranyl nitrate spectrum over two-millimicron wavelength intervals, in order to approximate the effect of raising the temperature, one obtains the banded spectrum shown in Fig. 4. (The lines of the "magnetic series" have been omitted because of the

[8] M. B. REYNOLDS and C. A. KRAUS, *J. Amer. Chem. Soc.* **70**, 1709 (1948).
[9] G. H. DIEKE and A. B. F. DUNCAN, *Spectroscopic Properties of Uranium Compounds*, McGraw-Hill, New York, 1949, p. 36.
[10] Ref. (9), p. 182.

observation[11] that their relative intensities fall off rapidly with increasing temperature.) The similarity of this curve, in the long-wavelength region, to that of trinitratouranyl ion in acetone is quite striking, and suggests that in the ion in solution the environment of the uranium atom is similar to that in the crystalline salt. In the isomorphous rubidium uranyl nitrate ($RbUO_2(NO_3)_3$), the three nitrate groups are known[12] to be arranged symmetrically about the uranium atom in a plane perpendicular to the O—U—O axis.

EXPERIMENTAL

Solvents

Merck reagent-grade acetone was treated with potassium permanganate, distilled, dried over anhydrous potassium carbonate, and redistilled through an efficient column. Other solvents were purified by careful fractional distillation.

Reagents

Uranyl nitrate hexahydrate was the ether-purified Malinckrodt product. Tetrabutylammonium nitrate, m.p. 118·5–119·5°, and tetrapropylammonium nitrate, decomposition point 260–261°, were prepared by the procedure of TUCKER and KRAUS.[5c]

Methyl isobutyl ketazine was prepared by refluxing 85 per cent hydrazine hydrate with a two-fold excess of methyl isobutyl ketone. The product boiled at 117–119° at 27 mm; 218° at 740 mm.[13]

Anal. calc. for $C_{12}H_{24}N_2$: N 14·27 per cent; found: N 14·19 per cent.

The amines used were redistilled Eastman products, except for 2-*n*-hexylpyridine, which was a fraction, b.p. 218–221° at 745 mm, from redistillation of the Reilly Chemical Co. product.

Analytical Procedures

Uranium was determined by a colorimetric procedure, using potassium ferrocyanide. Uranium-233, used as a tracer in some of the electrolytic transference experiments, was determined by alpha-counting in a 52 per cent geometry proportional counter.

Solvent Extraction Studies

A stock aqueous solution, 8*M* in ammonium nitrate, 0·4*M* in nitric acid, and 0·02*M* in uranyl nitrate hexahydrate, was used in all the experiments. Solutions of substituted ammonium nitrates in methyl isobutyl ketone were prepared either by weighing the anhydrous quaternary salt, or by adding equivalent amounts of the appropriate amine and concentrated nitric acid. Equal volumes of the aqueous and organic solutions were equilibrated, the phases were separated, and the concentration of uranium was determined for each phase.

Electrolytic Transference Experiments

The cell used was that described by MCLANE, DIXON, and HINDMAN,[14] except that the electrodes were of platinum. The cell compartments, which were separated by sintered glass disks, were filled with a methyl isobutyl ketone solution of the substituted ammonium salt; uranyl nitrate was added only to the contents of the centre compartment. In one experiment with 0·1*M* triethylammonium nitrate as the carrier electrolyte, and 0·01*M* uranyl nitrate hexahydrate in the centre compartment, electrolysis was continued for two hours at a current of 0·2 mA. It was found that 76 per cent of the uranium had migrated from the centre compartment; of this, 2·6 per cent was found in the cathode compartment and 97·4 per cent in the anode compartment. Since it was difficult to eliminate completely electro-osmotic effects when relatively high concentrations of uranyl nitrate were used, another experiment was performed in 0·05*M* tetrabutylammonium nitrate; the centre compartment contained,

[11] Ref. (9), p. 101.
[12] HOARD and STROUPE, quoted in Ref. (9), p. 15.
[13] A. MAILHE, *Bull. Soc. chim.* (4), **29**, 221, (1921), reports the boiling-point of this compound as 176°.
[14] C. K. MCLANE, J. S. DIXON, and J. C. HINDMAN, in *The Transuranium Elements, Research Papers*, G. T. SEABORG, J. J. KATZ, and W. M. MANNING, Eds., McGraw-Hill, New York, 1949, p. 358.

in addition, the uranyl nitrate prepared from 20 μg of uranium-233. Electrolysis for 2·5 h at 0·6 mA resulted in the migration of 83 per cent of the U^{233} out of the centre compartment, 99·9 per cent of which was found in the anode portion and only 0·1 per cent in the cathode portion. Electro-osmosis was negligible.

For comparison, an electrolysis was carried out in 1*M* aqueous nitric acid. After 20 h at 10 mA 43 per cent of the uranium had left the centre compartment; 99·8 per cent of this was found in the cathode portion and 0·2 per cent in the anode portion.

Spectrophotometric Measurements

Absorption spectra were measured with a Beckman model DU quartz spectrophotometer, using 1-cm Corex cells. Solutions were compared against the pure solvent. Where necessary, the readings were corrected for the slight absorption by reagents other than uranyl nitrate present in the solution. Solutions were prepared by accurately weighing the crystalline quaternary ammonium nitrate and uranyl nitrate hexahydrate and making up to volume with the solvent. Solutions of the other substituted ammonium nitrates were prepared from equivalent quantities of the amine and 16*M* aqueous nitric acid. Unless otherwise noted, the concentration of uranyl nitrate hexahydrate was 0·0200*M*. The temperature, which was not controlled, was in the range of 22° to 28°C.

Acknowledgement—The authors are indebted to Mr. H. H. HYMAN for a number of helpful suggestions.

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J. Inorganic and Nuclear Chemistry, 1956, Vol. 2, pp. 164–175. Pergamon Press Ltd., London

OBSERVATIONS ON THE RARE EARTHS—LXVII*

SOME OBSERVATIONS ON THE ABSORPTION SPECTRA OF NON-AQUEOUS SOLUTIONS OF SOME ACETYLACETONE CHELATES

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(*Received* 4 *August* 1955)

Abstract—Measurements of the absorption spectra of solutions of acetylacetonates of certain of the tripositive rare-earth metal ions in various non-aqueous solvents yield alterations in absorption intensities and resolutions of principal bands which support the view that the natures of these bands are determined by electrical fields imposed upon the 4*f* electrons by the associated anionic-type groups. For each species studied, only certain absorption bands are affected. The effects upon these bands are dependent upon the solvent used, but bear no simple relationship to dielectric constant. The absorption spectra of such solutions are in accord with Beer's law. Cryoscopic measurements show the solutes to be monomolecular in benzene and in carbon tetrachloride.

INTRODUCTION

THE absorption spectra of those tripositive rare-earth metal ions which show light absorption, unlike the spectra of other ionic species except those of the actinide elements, are distinguished by sharply defined and almost line-like absorption bands, which appear in the ultra-violet, visible, and near infra-red regions of the spectrum. Although the origins of all of these bands are incompletely understood, it is generally agreed that at least the stronger and highly characteristic bands arise from electronic transitions involving the 4*f* orbitals which are normally forbidden, but which are allowed by electric dipole effects.[1–4] The natures of such bands are thus determined by the electrical fields imposed upon the 4*f* electrons. In solution, such fields, as produced by distortion of the tripositive ions by surrounding ion atmospheres, are relatively weak in comparison with those existing in more rigidly ordered crystals. As a consequence, the absorption bands for salt solutions, although appearing in the same spectral regions as for the crystalline materials, are less complex and less intense than those found for the latter. Absolutely exact comparison is impossible, however, because of an incomplete knowledge of oscillator strengths for absorption bands in the crystalline compounds and of the dependence of band sharpness and intensity upon temperature. Superimposed to some extent upon these sharp absorption bands for the crystalline compounds are weaker satellite bands which appear to be vibrational in origin.[1, 4] These commonly disappear when the salt is dissolved.

If there is present in solution some anionic species which can associate closely with the rare-earth metal ion, the imposed field may be sufficiently intensified to permit

* For Part LXVI see: T. MOELLER, F. A. J. MOSS, and R. H. MARSHALL, *J. Amer. Chem. Soc.* **77**, 3182 (1955).

[1] L. J. F. BROER, C. J. GORTER, and J. HOOGSCHAGEN, *Physica* **11**, No. 4, 231 (1945).
[2] J. HOOGSCHAGEN, Doctoral Dissertation, University of Leiden, 1947.
[3] J. C. BRANTLEY, Doctoral Dissertation, University of Illinois, 1949.
[4] For a comprehensive summary, see D. M. YOST, H. RUSSELL, and C. S. GARNER, *The Rare-Earth Elements and Their Compounds*, John Wiley and Sons, Inc., N.Y., 1947, ch. 3.

enhanced absorptions at certain wavelengths.[3] Simple anionic species, however, do not associate sufficiently with these cations to produce sizable effects, but certain chelating groups may bond so firmly as to simulate in solution the conditions existing in crystalline compounds and lead to increases in both band intensities and complexities comparable with those found for the solid state.[3] Cases in point are the ethylenediaminetetraacetic acid[3, 5–8] and related[7–9] chelates in aqueous solution, and certain 5,7-dichloro-8-quinolinol chelates[10] in chloroform solutions. Enhanced stability of the chelate is reflected in more profound spectral alterations.

Since the β-diketone chelates of the tripositive rare-earth metal ions are among the more stable of the known complex species, it has been of interest to determine the changes in absorption spectra characterizing solutions of a number of these compounds. Data for typical acetylacetone chelates of ions giving well-defined spectra in the visible region are presented in this paper. Chelates involving other β-diketones will be described in a subsequent communication, together with comparisons among and interpretations of all the spectra. The absorption spectra of certain of the acetylacetone derivatives in various organic solvents have been studied by RADÖITCHITCH[11] but from a different point of view.

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EXPERIMENTAL

Materials employed. All rare-earth materials were from the University of Illinois stocks. Praseodymium, neodymium, and samarium materials were essentially free from other rare-earth elements. On the basis of absorption analyses,[12] the holmium sample contained 10 per cent Ho_2O_3 with less than 0·1 per cent Er_2O_3 and the erbium sample 88·5 per cent Er_2O_3 with less than 1 per cent Ho_2O_3—Tm_2O_3. The balance of material in these two samples was yttrium, which gives no absorption bands.[12] The organic solvents employed were of reagent quality and were dried with either sodium metal or freshly calcined calcium oxide just prior to use. Reagent quality acetylacetone was distilled just before use.

Apparatus. All absorption spectra were measured at *c.* 25°C with either a Beckman Model-DU quartz spectrophotometer or a Cary Recording Spectrophotometer Model 11, as previously described,[5, 10, 13] using demountable cells with quartz windows. Hydrogen-ion concentrations were determined with a Beckman Model-G pH meter. Cryoscopic measurements were made according to the standard technique.

Preparation of acetylacetone chelates. The procedure employed was a modification of that recommended by STITES, MCCARTY, and QUILL.[13] Oxide samples (1·5–4·5 g) were dissolved in dilute hydrochloric-acid solution, and excess acid was removed by evaporation. The resulting chloride solutions were added to 100 ml volumes of 1 : 1 water-purified dioxane solution containing a slight excess of acetylacetone. The pH values of the vigorously stirred solutions were adjusted by the dropwise addition of aqueous ammonia to just below those for hydrous hydroxide or oxide precipitation[14] over 20-h periods. The crystalline products were removed by filtration, washed with successive portions of anhydrous ethanol, and dried over magnesium perchlorate in a vacuum desiccator. Conditions for precipitation, as well as data obtained in characterizing the compounds in terms of melting-points and micro-analyses, are given in Table 1.

Molecular-weight determinations. Molecular weights were determined by the standard cryoscopic

[5] T. MOELLER and J. C. BRANTLEY, *J. Amer. Chem. Soc.* **72**, 5447 (1950).
[6] F. A. J. MOSS, Doctoral Dissertation, University of Illinois, 1952.
[7] R. C. VICKERY, *J. Chem. Soc.* 421 (1952).
[8] L. HOLLECK and D. ECKHARDT, *Z. Naturforsch.* **8a**, 660 (1953); **9a**, 347 (1954); **9b**, 274 (1954).
[9] R. C. VICKERY, *J. Chem. Soc.* 385 (1954).
[10] T. MOELLER and D. E. JACKSON, *Anal. Chem.* **22**, 1393 (1950).
[11] M. RADÖITCHITCH, *Ann. chim.* [11], **13**, 5 (1940).
[12] T. MOELLER and J. C. BRANTLEY, *Anal. Chem.* **22**, 433 (1950).
[13] J. G. STITES, C. N. MCCARTY, and L. L. QUILL, *J. Amer. Chem. Soc.* **70**, 3142 (1948).
[14] T. MOELLER and H. E. KREMERS, *J. Phys. Chem.* **48**, 395 (1944).

procedure, using redistilled benzene or carbon tetrachloride as solvent. Summarized in Table 2 are results as calculated from the relationship

$$M = 1000\,K_f(g/G\Delta t_f)$$

where M is the molecular weight, K_f the freezing-point constant for the solvent employed, g the weight in grams of the solute, G the weight in grams of the solvent, and Δt_f the observed freezing-point lowering for the solution.

TABLE 1.—PREPARATION AND PROPERTIES OF ACETYLACETONE CHELATES

Chelate	pH for preparation	Analyses				Melting-point °C	Colour
		per cent C		per cent H			
		Calcd.	Found	Calcd.	Found		
$Pr(C_5H_7O_2)_3$	6·5	41·05	40·86	4·83	4·94	144–145	green
$Nd(C_5H_7O_2)_3$	6·5	40·70	40·63	4·80	4·96	144–145	pink
$Sm(C_5H_7O_2)_3$	6·5	40·20	39·96	4·78	4·83	144–145	yellow
$Ho(C_5H_7O_2)_3$[a]	5·5	45·72	44·26	5·34	5·46	—	white
$Er(C_5H_7O_2)_3$[b]	6·0	39·48	39·27	4·67	4·73	142–144	pink

[a] 10 per cent $Ho(C_5H_7O_2)_3$—90 per cent $Y(C_5H_7O_2)_3$.
[b] 88·5 per cent $Er(C_5H_7O_2)_3$—11·5 per cent $Y(C_5H_7O_2)_3$.

TABLE 2.—MOLECULAR WEIGHT DETERMINATIONS FOR ACETYLACETONE CHELATES

Solute		Solvent			Solution	Molecular weight	
Chelate	Weight g	Formula	Weight g	K_f °C	Δt_f °C	Calc.	Found
$Pr(C_5H_7O_2)_3$	0·0998	C_6H_6	24·519	5·12	0·050	438	423
	0·1830	C_6H_6	24·519	5·12	0·098		429
	0·1043	CCl_4	26·144	32·30	0·282		457
$Nd(C_5H_7O_2)_3$	0·0582	C_6H_6	20·990	5·12	0·033	442	434
	0·1372	C_6H_6	20·990	5·12	0·076		439
	0·1246	CCl_4	28·965	32·30	0·308		451
$Sm(C_5H_7O_2)_3$	0·1003	C_6H_6	23·414	5·12	0·052	448	421

RESULTS AND DISCUSSION

Properties of chelates. The acetylacetone chelates obtained in this study were characterized by ready solubility in a variety of organic solvents. This fact, coupled with the analytical data in Table 1, suggests that they were anhydrous compounds free from basic derivatives. That they were apparently monomolecular in both benzene and carbon tetrachloride is at variance with observations of dimerization as reported by BILTZ[15] and employed[16] for interpretations of the absorption spectrum of the europium compound, although this difference may represent a concentration effect.[15] Protection of solutions of the chelates in organic solvents from moisture, heat, and light was essential to avoid decompositions.

Absorption spectra. Typical absorption spectra for solutions of the chelates investigated in various organic solvents are summarized in Figs. 1–8. In each case only those regions of the spectrum which were appreciably affected by the chelating agent are included; and, for comparison, data for an aqueous salt solution are given.[17]

[15] W. BILTZ, *Ann.* **331**, 334 (1904).
[16] S. FREED, S. I. WEISSMAN, and F. E. FORTESS, *J. Amer. Chem. Soc.* **63**, 1079 (1941).
[17] All curves are plotted in terms of the absorptivity a, which is defined by the relationship $a = (\log_{10} I_0/I)/cb$, where c is given as grams of rare-earth metal per litre and b as centimetres.

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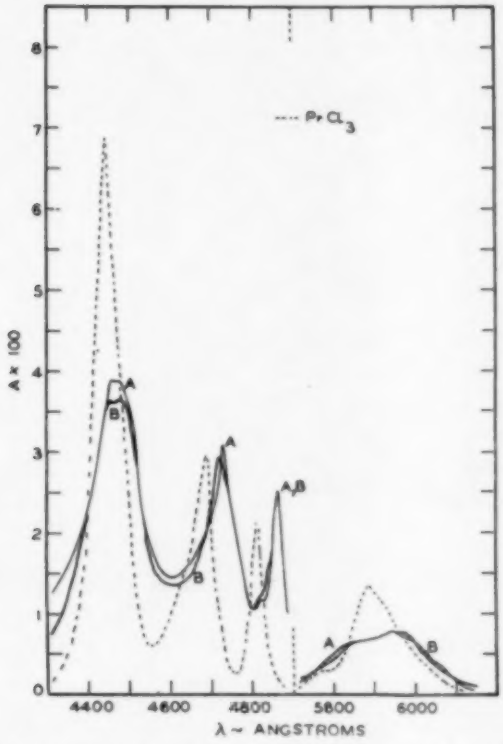

FIG. 1.—Absorption spectra of praseodymium acetylacetonate solutions: A benzene, B chloroform.

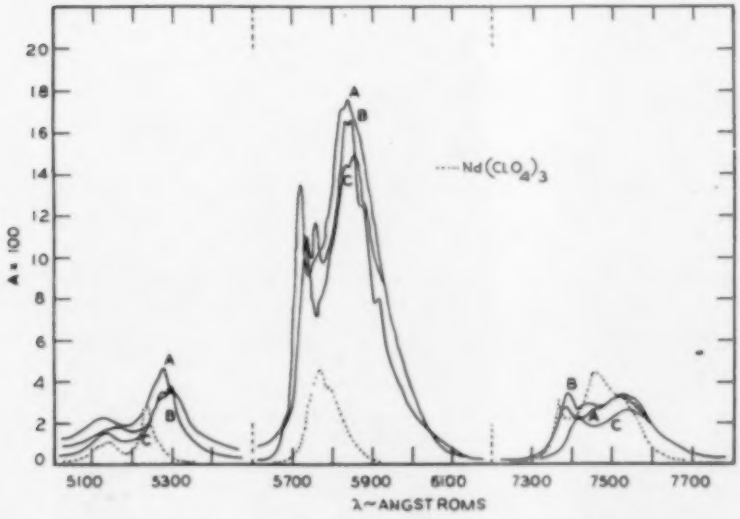

FIG. 2.—Absorption spectra of neodymium acetylacetonate solutions: A ethanol, B acetone, C methanol.

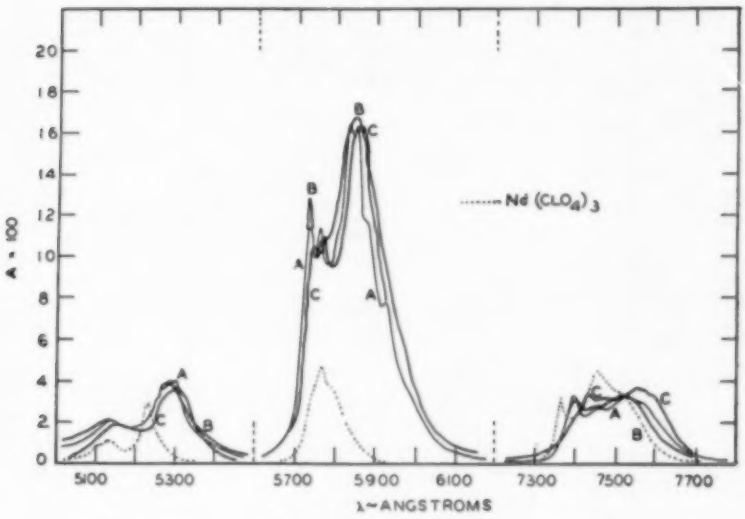

FIG. 3.—Absorption spectra of neodymium acetylacetonate solutions: A chloroform, B *n*-butanol, C toluene.

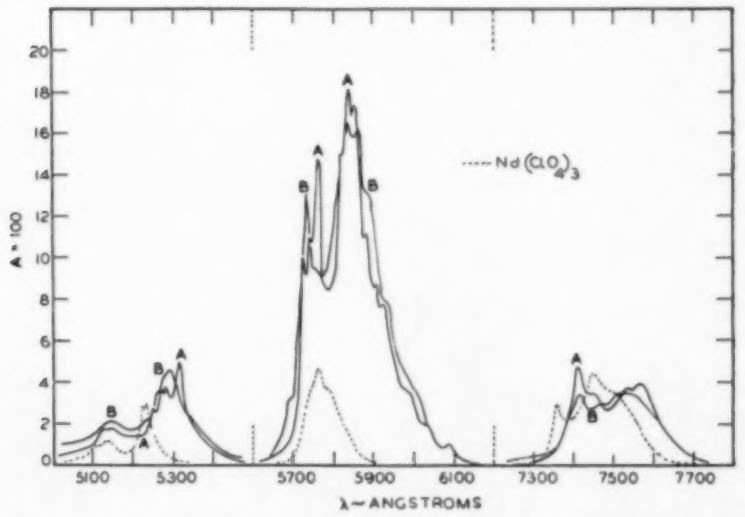

FIG. 4.—Absorption spectra of neodymium acetylacetonate solutions: A benzene, B carbon tetrachloride.

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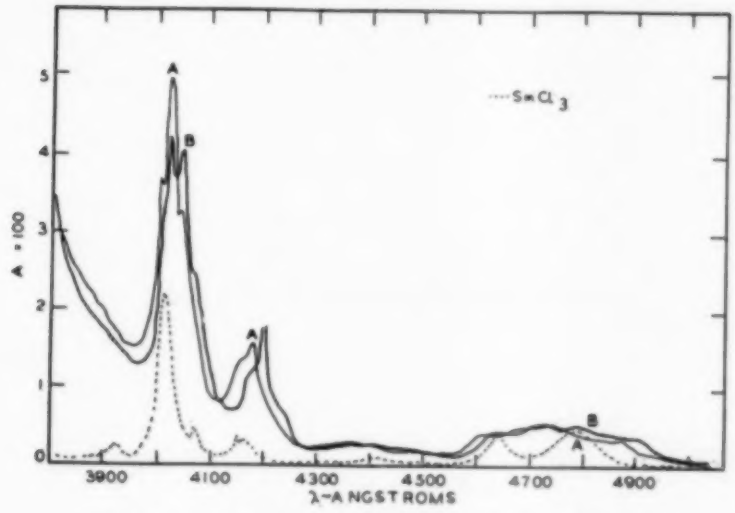

FIG. 5.—Absorption spectra of samarium acetylacetonate solutions: A chloroform, B benzene.

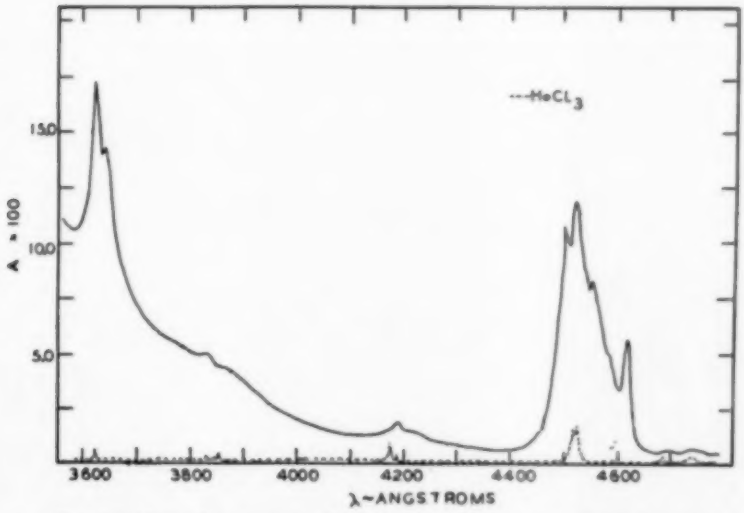

FIG. 6.—Absorption spectrum of holmium acetylacetonate solution in benzene.

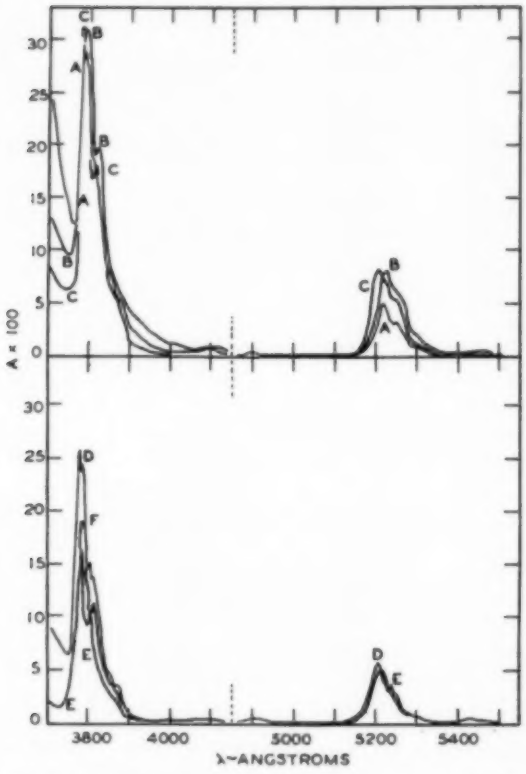

FIG. 7.—Absorption spectra of erbium acetylacetonate solutions: A toluene, B methanol, C *n*-butanol, D carbon tetrachloride, E ethanol, F chloroform.

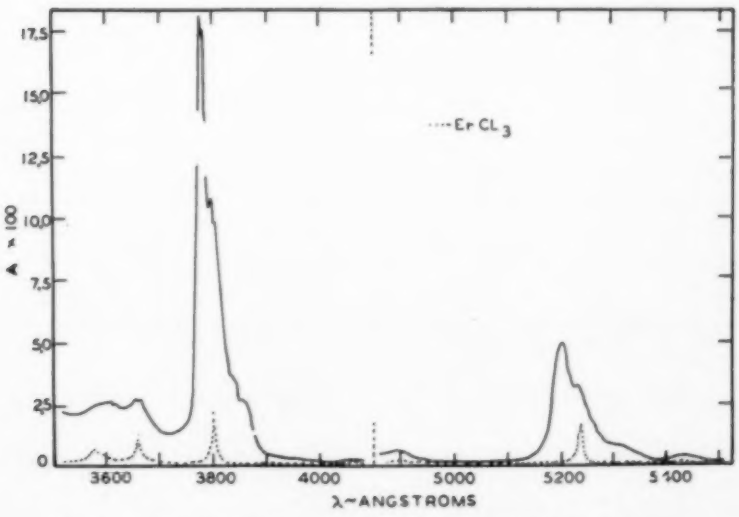

FIG. 8.—Absorption spectrum of erbium acetylacetonate solution in benzene.

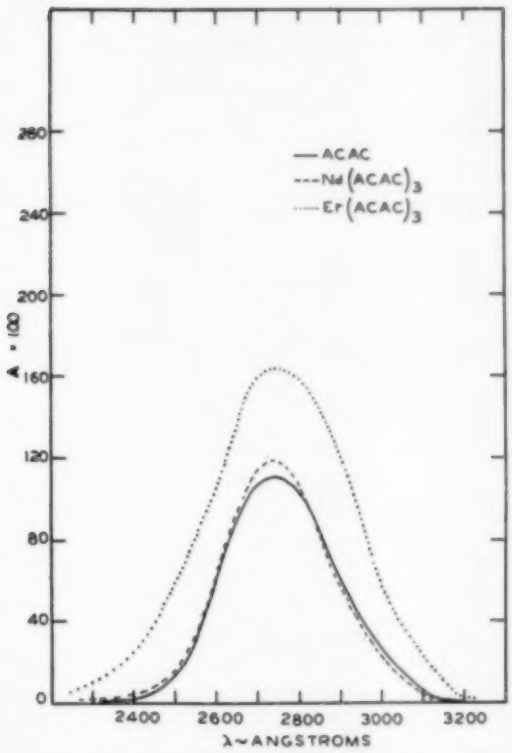

FIG. 9.—Absorption spectra of chloroform solutions.

Measurements at wavelengths below *c.* 3600 Å were precluded by the intense ultraviolet absorption of the acetylacetonate structure in the 2740-Å region, as shown in Fig. 9. Numerical data characterizing the rare-earth absorption bands are summarized in Tables 3–7, and those describing the acetylacetone structure are given in Table 8.

Although the most striking effects in terms of absorption-band intensifications, displacements, and resolutions might appear to be in the neodymium and erbium spectra, equally important effects of the same types may be distinguished in the samarium and holmium spectra. With praseodymium, however, chelate-formation decreases absorption intensities and leads to wavelength displacements, but is without detectable effect upon band complexities. These results all parallel closely those obtained for aqueous solutions containing ethylenediaminetetraacetate,[3,5,6] those obtained for chloroform solutions of 5,7-dichloro-8-quinolinol chelates,[10] and, except for praseodymium, those obtained by HOLLECK and ECKHARDT[8] for aqueous solutions containing a variety of complexing agents. In that they show resolution effects for cations other than neodymium and erbium, they are at variance with VICKERY's data.[7] Distinguishable in certain of the spectra, notably that of the neodymium chelate in benzene, are well-developed vibrational fine structures. Although for a given cation the greatest band resolution seems to be obtained in solvents of low dielectric constant, no direct relationship to dielectric constant could be devised.[11]

In spectra where bands were intensified or resolved, the greatest effects appeared

with only a limited number of bands, e.g., the 5745-Å neodymium absorption band and the 3792-Å erbium absorption band, suggesting that only certain electronic transitions involving the 4*f* orbitals can be affected by chelate formation. The observed broadening and wavelength displacements of these bands are in accord with the view[3] that these result from enhanced holohedric potentials,[3,18] i.e., enhanced

TABLE 3.—ABSORPTION BANDS OF PRASEODYMIUM COMPOUNDS

$PrCl_3$		$Pr(C_5H_7O_2)_3$			
Water		Chloroform		Benzene	
λ_{max}[a]	ε[b]	λ_{max}	ε	λ_{max}	ε
4445	9·66	4457	5·46	4458	5·44
4690	4·21	4723	4·16	4730	4·33
4822	3·02	4861	3·44	4863	3·55
5885	1·89	5933	1·10	5944	1·15

[a] Wavelength of maximum absorption in Ångströms.
[b] Molar absorptivity.

TABLE 4.—ABSORPTION BANDS OF NEODYMIUM COMPOUNDS

$Nd(ClO_4)_3$ water		$Nd(C_5H_7O_2)_3$															
		Methanol		Ethanol		Acetone		*n*-Butanol		Chloroform		Toluene		Benzene		Carbon tetrachloride	
λ_{max}[a]	ε[b]	λ_{max}	ε	λ_{max}	ε	λ_{max}	ε	λ_{max}	ε	λ_{max}	ε	λ_{max}	ε	λ_{max}	ε	λ_{max}	ε
5125	1·72	5145	2·60	5130	3·18	5130	2·16	5126	3·31	5135	2·91	5150	2·94	5120	2·45	5134	2·80
														5245	3·79	5255	4·59
														5265	5·18		
5218	4·33			5278	6·56	5270	4·96	5278	7·57	5275	5·56			5279	5·48		
		5294	5·45			5292	5·51			5300	5·75	5300	5·22	5311	7·21	5292	6·09
		5727	1·61	5719	19·5	5731	14·9	5725	14·6					5721	14·5		
										5733	16·5	5744	16·2	5739	15·9	5734	16·9
						5755	16·8	5760	13·6	5759	16·5	5764	16·9	5761	20·8		
5745	6·66	5826	20·4			5828	23·8			5830	23·7	5848	23·6	5840	26·2	5841	21·2
		5851	21·6	5838	25·4	5843	24·0	5840	20·4	5850	23·4	5863	22·9	5856	25·2	5859	21·1
														5880	16·2		
														5908	12·7		
						5913	15·9			5923	11·1			5923	10·4		
														6086	1·52		
7330	3·52	7412	3·14	7380	3·96	7385	4·94	7392	3·26	7392	4·67	7428	5·40	7419	6·34	7408	4·54
						7430	4·20										
7420	6·59							7502	4·14	7453	3·81			7445	5·04		
		7534	3·07	7510	3·74	7522	4·91										
										7521	4·65	7550	5·37	7530	5·23		
														7568	5·74	7571	4·69

[a] Wavelength of maximum absorption in Ångströms.
[b] Molar absorptivity.

potential effects of the static symmetric fields imposed upon the metal ions by the coulombic fields of the surrounding anions. Still further broadening to produce actual band-splitting or resolution could then result from enhanced symmetry as a sort of internal Stark effect. Furthermore, the observed increases in absorption intensities of these bands are in accord with the view[3] that they result from enhanced hemihedric potentials,[3,18] i.e., enhanced potential effects of the unsymmetric fields imposed upon

[18] J. H. VAN VLECK, *J. Phys. Chem.* **41**, 67 (1937).

TABLE 5.—ABSORPTION BANDS OF SAMARIUM COMPOUNDS

$SmCl_3$		$Sm(C_5H_7O_2)_3$			
Water		Chloroform		Benzene	
λ_{max}[a]	ε[b]	λ_{max}	ε	λ_{max}	ε
		4008	5·51		
4020	3·14	4023	7·35	4024	6·38
		4046	4·90	4048	6·08
4072	0·61				
4150	0·46	4178	2·35	4199	3·54
4175	0·42				
		4603	0·62		
4640	0·54	4680	0·72	4726	0·78
		4750	0·80	4795	0·78
4790	0·57	4875	0·50	4900	0·67

[a] Wavelength of maximum absorption in Ångströms.
[b] Molar absorptivity.

TABLE 6.—ABSORPTION BANDS OF HOLMIUM COMPOUNDS

$HoCl_3$		$Ho(C_5H_7O_2)_3$	
Water		Benzene	
λ_{max}[a]	ε[b]	λ_{max}	ε
3622	—	3620	
3823	—		
3854	—	3828	—
3900	—		
4162	1·85		
4221	0·66	4180	—
		4497	17·5
4512	2·82	4520	19·5
4525	2·85	4551	13·4
		4615	9·0
4685	0·68		
4741	0·69		
4806	0·42		
4858	1·32		
5371	3·48	5380	1·78
5438	1·22		
6409	2·26	6400	0·83
6526	7·84		
6562	7·84		

[a] Wavelength of maximum absorption in Ångströms.
[b] Molar absorptivity.

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TABLE 7.—ABSORPTION BANDS OF ERBIUM COMPOUNDS

$ErCl_3$		$Er(C_5H_7O_2)_3$													
Water		Methanol		Ethanol		*n*-Butanol		Chloroform		Toluene		Benzene		Carbon tetrachloride	
λ_{max} [a]	ε [b]	λ_{max}	ε	λ_{max}	ε	λ_{max}	ε	λ_{max}	ε	λ_{max}	ε	λ_{max}	ε	λ_{max}	ε
3559	0·73														
3590	0·42			3600	—			3610	—			3609	—		
3642	1·29			3650	—			3660	—			3655	—		
3792	4·00	3789	36·0	3778	25·1	3781	29·8	3780	38·6	3782	29·3	3776	29·6	3780	35·2
		3816	22·1	3806	14·8	3811	16·1	3810	19·3			3779	28·5	3785	32·6
												3795	16·7	3803	18·7
												3803	15·0	3810	16·9
4850	0·56														
4870	1·21														
4910	0·59	4900	0·79	4890	0·51	4898	0·57	4895	1·02	4891	0·82	4882	0·79	4880	0·80
5228	1·98	5215	12·8	5203	8·18	5206	9·52	5206	11·0	5215	8·56	5201	8·00	5208	9·25
								5245	6·49	5246	8·44	5224	5·09	5231	6·01

[a] Wavelength of maximum absorption in Ångströms.
[b] Molar absorptivity.

TABLE 8.—ABSORPTION BANDS OF ACETYLACETONE STRUCTURE IN CHLOROFORM SOLUTION

Solute	λ_{max} Å	ε
$C_5H_8O_2$	2741	11,080
$Pr(C_5H_7O_2)_3$	2739	11,210
$Nd(C_5H_7O_2)_3$	2739	11,700
$Sm(C_5H_7O_2)_3$	2740	12,190
$Er(C_5H_7O_2)_3$	2735	16,200

TABLE 9.—BEER'S LAW ADHERENCE OF SOLUTIONS OF ACETYLACETONE CHELATES

Chelate	Concentration	Ethanol		Acetone		Chloroform		Benzene		Carbon tetrachloride	
	g metal/l.	λ Å	ε_{av}	λ Å	ε_{av}	λ Å	ε_{av}	λ Å	ε_{av}	λ Å	ε_{av}
$Pr(C_5H_7O_2)_3$	1·290–2·580					4457	5·64	4458	5·46		
$Nd(C_5H_7O_2)_3$	0·279–1·116	5838	22·82	5843	21·62	5830	21·37	5840	23·61		
$Sm(C_5H_7O_2)_3$	1·062–4·250					4023	7·49	4024	6·48		
$Ho(C_5H_7O_2)_3$	0·302–1·208							4520	18·98		
$Er(C_5H_7O_2)_3$	0·156–0·626	3778	25·55			3780	39·08	3776	29·60	3780	35·50
	0·313–0·939	5203	8·14			5206	11·05	5201	8·00	5208	9·25

4*f* orbitals by distortion of the cation by the surrounding anions. That these effects are so pronounced with the acetylacetone chelates is an indication of the stabilities of these complexes with respect to their components and of the maintenance of these chelate structures in solution.

The major absorption peaks of the various acetylacetonates obey Beer's law over rather wide concentration ranges for a variety of solvents, as shown by the typical data summarized in Table 9. It follows from comparisons of these data with those for aqueous systems[12] that spectrophotometric determinations may be made at lower concentration levels with the acetylacetonates in all cases studied except praseodymium.

Acknowledgement—Grateful appreciation for support of this investigation is expressed to the Office of Naval Research and to E. I. duPont de Nemours and Company.

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J. Inorganic and Nuclear Chemistry, 1956, Vol. 2, pp. 176–179. Pergamon Press Ltd., London

FAST SEPARATIONS OF CATIONS USING ASCENDING PAPER CHROMATOGRAPHY*

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(*Received* 5 *August* 1955)

Abstract—Separations of microgram quantities of radioactive mercury, thallium, bismuth, and lead, and of non-radioactive platinum, gold, copper, nickel, cobalt, iron, cadmium, silver, and palladium, in from 2 to 20 min, have been achieved using a new method of ascending paper chromatography with acetone containing various complexing agents as the developer. The new technique involves the use of thick absorbent paper having high wettability, a developer of high wetting power, and, in particular, an atmosphere which is supersaturated with vapours of the solvent.

INTRODUCTION

USING ascending paper chromatography, cation separations normally require more than 10 h and frequently as much as 48 h. Moderately rapid separations (1 to 4 h) have been reported, using the descending paper technique[1] or electrochromatography.[2] In order to apply chromatographic methods to the study of short-lived radioactive nuclides formed in fission, spallation, or by radioactive decay of long-lived nuclides, the separation time must be reduced as much as possible. Chromatography is also well suited to valence-state separations in the study of chemical states formed from nuclear processes, as examples given below will show. Advantages of chromatography over some conventional methods lie in the facts that decontamination factors can be exceptionally high, the technique often is less laborious, and the desired element may be separated from all others present or a mixture of activities resolved carrier-free in a single step.

We have developed a technique by which separations may be accomplished in from 2 to 20 min, using ascending paper chromatography, which has the advantage over the descending method in greater simplicity and ease of operation. The method involves the use of a developer of high wetting power together with paper having high wettability in an atmosphere which is *supersaturated* with vapours of the solvent.

Acetone, containing various amounts of complexing agents (see Table 1), was found most suitable as the developer; in the absence of complexing agents, however, acetone gave poor separations in which most zones appeared with long, overlapping tails. Aqueous solutions of various complexing compounds also were found to give clean separations under similar conditions, but the separation time was somewhat longer.

EXPERIMENTAL

The most suitable paper found for producing fast and reproducible separations was Eaton-Dikeman Grade-301, 0·1-in thick, which had been purified according to the method of SATO, NORRIS, and STRAIN,[3] which involves downward percolation with nitric acid, acetic acid, and water. Whatman No. 1 paper without washing will give separations normally in 1 to 2 h under identical conditions.

* Supported in part by the U.S. Atomic Energy Commission.

† Part of a thesis presented to the University of Arkansas in partial fulfilment of the requirements for the M.S. degree (1956).

[1] G. CARLESON, *Acta Chem. Scand.* **8**, 1673 (1954).

[3] H. H. STRAIN and J. C. SULLIVAN, *Anal. Chem.* **23**, 8161 (1951).

All experiments were carried out in 10-cm diameter glass tubes about 50 cm long placed erect in a 1-litre beaker containing the developer solution. A rubber stopper, containing both a glass hook for suspending the paper strip and two 6-mm glass vapour tubes, was used to seal off the tube. Solvent vapours were introduced continuously by passing a small stream of air through a flask containing the boiling solvent connected to the vapour inlet of the glass chamber.

About 10 μl of a solution containing 5 to 10 μg of the cation to be studied was applied to the paper, so that when suspended in the chamber the spot would be about 1 cm above the surface of the developer. With mercury, thallium, bismuth, and lead were used radioactive Hg^{203}, Tl^{204}, RaE, and Pb^{210} respectively, either at tracer concentrations or carrier-free. Prior to suspending the paper strip, the chamber was supersaturated with solvent vapours, as described above. In practice the chamber is ready for use about 5 to 10 min after the solvent vapours are first introduced. Under these conditions, acetone ascends the first 20 cm of Eaton-Dikeman Grade-301 paper in about 15 min, whereas 1½ to 2 h are required for acetone to ascend the same distance on Whatman No. 1 paper. After a distance suitable for a separation is reached (from 5 to 20 cm, depending on the R_F values for the particular developer system), the strip is removed from the chamber and either streaked with a suitable reagent to indicate the presence of the zones or scanned with a counter.

The streaking reagents[4] used to locate the zones were as follows: diphenylcarbazide (0·05 per cent in ethanol) for Hg^{+}, Hg^{++}, and Tl^{+3}; potassium iodide (5 per cent solution) for Pt^{+4}, Pd^{++}, Au^{+3}, Hg^{+}, Hg^{++}, Tl^{+}, Tl^{+3}, Pb^{++}, and Bi^{+3}; sodium sulphide (5 per cent solution) for Cd^{++}, Cu^{+}, Cu^{++}, Co^{++}, Ni^{++}, Pb^{++}, Au^{+3}, Pt^{+4}, Tl^{+}, Tl^{+3}, Bi^{+3}, Fe^{++}, Fe^{+3}, and Ag^{+}; dimethylaminobenzalrhodamine (0·03 per cent in ethanol) for Hg^{+}, Hg^{++}, and Ag^{+}.

The R_F value tabulated in Table 1 is the ratio of the distance of the leading edge of a zone to the distance of the solvent front, both measured from the midpoint of the original spot. Each value in Table 1 represents the average of five or more independent runs.

In order to obtain separations which could be reproduced consistently, several variables were investigated to ascertain their relative influence on the R_F value:

1. *Chromatographic paper.* The R_F values listed in Table 1 were obtained using Eaton-Dikeman Grade-301 paper, 0·1-in thick, which was purified by allowing 500 ml of 1M nitric acid to descend each 7·5 cm × 50 cm strip, followed by 1 litre distilled water, 500 ml of 1M acetic acid, and distilled water until neutral; this was repeated a second time. Grade-301 paper which is not purified results in tailing out of the zones, giving poor separations. Whatman No. 1 paper may be used satisfactorily without purification, but the separation time is longer.

2. *Concentration of complexing agents.* Concentrations of the various complexing agents in acetone (Table 1) were chosen, so that minor variations in concentration have little or no effect upon the R_F value.

3. *Saturation of the atmosphere.* The rate at which the solvent in a particular grade of paper ascends, depends directly upon the extent to which the atmosphere is saturated with solvent vapours. R_F values may be considerably greater if the chamber is not saturated due to evaporation from the solvent front during ascension; thus, the solvent front may slow down when the zones are still moving. By providing a supersaturated atmosphere, this troublesome variable is removed.

4. *pH of the original solution.* It was found that the R_F value was neither affected by the pH nor by the acid or base used to adjust the pH, provided a precipitate was not formed.

5. *Foreign ion concentration.* The R_F value generally was found to be independent of foreign cations present at various concentrations. However, R_F values have been observed to be altered as much as 5 per cent for developer systems I, II, and VIII in Table 1, separating carrier-free Pb^{210} from Ra-DEF solutions when as much as 50 μg of bismuth carrier is present. Previous investigators[6] have reported a similar effect with Ra-DEF separations.

DISCUSSION

Using thick absorbent paper with fast-wetting solvent, microgram concentrations of Pt, Au, Cu, Ni, Co, Fe, Cd, Ag, Pd, Hg, Tl, Bi, and Pb may be quantitatively separated within 2 to 15 min. The time of separation is only 2 to 4 min providing a

[3] Sato, Norris, and Strain, *Anal. Chem.* **27**, 521 (1955).
[4] F. Feigl, *Spot Tests*, Vol. I, Elsevier Publishing Co. (1954).
[5] W. J. Frierson and J. W. Jones, *Anal. Chem.* **23**, 1447 (1951).

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TABLE 1.—R_F VALUES OF VARIOUS CATIONS ON EATON-DIKEMAN GRADE-301 PAPER, USING VARIOUS DEVELOPER SYSTEMS

Cations	Developer Systems*									
	I	II	III	IV	V	VI	VII	VIII	IX	X
Pd^{++}	0·91	0·82	0·98	0·92	0	0·95	0·88	0·86	0·83	
Ag^{+}	0	0·40	0·44	0·45	0	0·37	0	0·23	0·96	
Cd^{++}	0·63		0·76	0·68	1·0	0·45	0·46	0·33	0·75	
Fe^{++}	0·76	0·80	0·24	0·52	0	0·73	0	0·88	0·81	
Fe^{+3}	0·76	0·70	0	0	0	0	0	0	0·85	
Co^{++}	0·33	0·80	0·64	0·55	0	0·40	0·40	0·26	0·93	
Ni^{++}	0	0·62	0	0·17	0	0	0	0	0·91	
Cu^{+}	0·46	0·60	0	0	0	0	0	0·21	0·79	
Cu^{++}	0·46	0·60	0	0	0	0	0	0	0·97	
Bi^{+3}	0·93	0·93	0·98	0·96	1·0	0·98	0·92	0·91	0·91	0
Pb^{++}	0·48	0·16	0	0·35	0	0	0·23	0	0·81	0·7
Tl^{+}	0·11	0·26	0·26	0·08	0	0	0	0	0·71	0·4
Tl^{+3}	0	0	0·26	0·45	0	0	0	0	0·70	0·4
Hg^{+}	0·96		0·80	0·83		0·13	0·77	0·74	1·0	0·3
Hg^{++}	0·80		0·82	0·83		0·13	0·77	0·74	1·0	0·3
Au^{+3}	1·0	1·0	1·0	1·0	1·0	1·0	1·0	1·0	0·71	0
Pt^{+4}	0·89	1·0	1·0	0·92	1·0	1·0	0·88	0·80	0·89	

* The developer systems used in the experiments above are indicated as follows:

I. 5 per cent of 6N HCl—95 per cent acetone.
II. 5 per cent of 0·5N HCl—95 per cent acetone.
III. 10 per cent of a 5 per cent tartaric acid solution—90 per cent acetone.
IV. 10 per cent of a 5 per cent Na_2HPO_4 solution—90 per cent acetone.
V. 20 per cent methyl acetate—80 per cent acetone.
VI. 5 per cent of a 10 per cent antipyrine solution—95 per cent acetone.
VII. 5 per cent of a 5 per cent solution of thioacetamide—95 per cent acetone.
VIII. 5 per cent of glacial acetic acid—95 per cent acetone.
IX. 5 per cent tartaric acid solution (aqueous).
X. Water saturated with aniline.
(Note: Percentages are by volume except in the case of solids, where they are by weight.)

developer system is chosen (see Table 1) which gives a zero R_F value for the neighbouring elements and an R_F value $\geq 0{\cdot}5$ (preferably 1·0) for the element being separated.

Examples of separations which are possible include the following:

1. Fifty micrograms or less of Cd^{++} can be separated within 2 min from almost macro concentrations of Ag^{+} and Pd^{++} when the developer chosen is 20 per cent methyl acetate—80 per cent acetone (see Table 1).
2. Tracer concentrations of Pb^{++} may be separated within 5 min from macro concentrations of bismuth by employing water saturated with aniline as the developer (see Table 1).
3. Tracer concentrations of bismuth may be separated within 2 min from macro concentrations of lead by employing a mixture of 20 per cent methyl acetate—80 per cent acetone as the developer.
4. Microgram concentrations of Au^{+3} may be separated within 2 min from macro concentrations of lead and/or thallium by using as a developer a mixture of 5 per cent thioacetamide—95 per cent acetone.

5. Tracer concentrations of thallium may be separated within 6 min from macro concentrations of gold using water saturated with aniline as the developer.
6. Microgram quantities of nickel may be separated from macro concentrations of cobalt within 3 min using 10 per cent tartaric acid—90 per cent acetone.
7. Tracer concentrations of Hg^{++} may be separated from macro quantities of lead and thallium using 5 per cent glacial acetic acid—95 per cent acetone.
8. Ferric iron may be separated from ferrous iron within 3 min using 5 per cent antipyrine solution (10 per cent)—95 per cent acetone.
9. Thallium(III) may be separated from thallium(I) in less than 12 min using 10 per cent of a 5 per cent Na_2HPO_4 solution with 90 per cent acetone as the developer.

Separation of the valence states of iron and thallium by this technique may be useful in the investigation of exchange reactions or of chemical states resulting from nuclear transformations requiring a rapid analytical method. Developer systems, which cause all elements to be strongly absorbed with the exception of one which moves with the solvent front, are ideal for obtaining carrier-free separations of one element from various concentrations of other elements. It is clear that this fast technique will be of application in many problems of separation of radioactive elements.

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J. Inorganic and Nuclear Chemistry, 1956, Vol. 2, pp. 180–183. Pergamon Press Ltd., London

NUCLEAR RECOIL AS A MEANS OF FISSION PRODUCT SEPARATION*

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(*Received* 9 *August* 1955)

Abstract—It has been demonstrated that, by use of a suitable heterogeneous system, the nuclear recoil of fission products can be used to effect their complete separation from the parent fissile material. The potentialities of this simple technique are briefly discussed.

McMILLAN's pioneering study[1] of the recoil of uranium fission products led to his 1939 discovery of neptunium activity. He had irradiated a thin film of uranium oxide with cyclotron neutrons and found that most of the fission products had recoiled out of it. This separation made it possible to recognize the strong 2·3-day activity of the Np^{239} that had been left behind. Since that time the momentum properties of fission products have been intensively investigated with a view to determining kinetic energies, angular distributions, and modes of energy loss. However, little further attention appears to have been given to the practical potentialities inherent in fission recoil for the development of important separation techniques.[2]

If a fission reaction is carried out in particles of fissile materials with maximum dimensions smaller than the range of the fission products, these products will necessarily recoil out of the parent material. On the other hand, the heavier nuclei formed by neutron capture and beta decay will have a very much shorter recoil range and will remain within the original particle unless it is extremely small. This means that in a suitable heterogeneous system the fission products will completely separate themselves from the actinides, eliminating the need for complex chemical processing. This paper reports on a simple experiment carried out to test the practicability of such a procedure.

EXPERIMENTAL

The minimum range of fission fragments from plutonium is 1·9 cm in air[3] (760 mm 15°C). From this it can readily be calculated that the equivalent minimum range in U_3O_8 is 8 microns. Assuming that the U^{235} fission recoils do not differ significantly from those from plutonium, we can predict that all fission products produced in U_3O_8 will recoil out of any particle smaller than 8 microns.

Fine U_3O_8 particles were produced by grinding in a mortar and applying a simple sedimentation procedure. The particles thus produced were fairly uniform and somewhat less than 1 μ in diameter. Despite this small size, the U_3O_8 still tended to settle out of a water suspension. In order to maintain a suspension without having to provide a means of agitation while irradiating, the particles were added to a hot 3 per cent gelatin solution which was then chilled with stirring to produce a uniform distribution of U_3O_8 in the gel. About 10 ml of such a gel containing approximately 3 mg of U_3O_8 were irradiated in the central portion of the Brookhaven reactor for about a minute.

After irradiation the gel was liquefied by warming in a hot-water bath. The mixture was centrifuged, and portions of the supernate were removed to aluminium planchets for drying and counting.

* Research performed under the auspices of the U.S. Atomic Energy Commission.

(1) E. McMILLAN, *Phys. Rev.* **55**, 510 (1939).
(2) F. JOLIOT used a technique very similar to that of McMILLAN to obtain pure fission products which had recoiled into filter paper from layers of uranium oxide. *Compt. Rend.* **218**, 733 (1944).
(3) S. KATCOFF, J. A. MISKEL, and C. W. STANLEY, *Phys. Rev.* **74**, 631 (1948).

The solid U_3O_8 in the bottom of the centrifuge cone was washed three times with water, then transferred to an aluminium planchet for drying and counting. The counters used were end-window gas-flow proportional beta counters.

Pure 3 per cent gelatin solution containing no uranium was similarly irradiated and counted. The activity of this control sample never exceeded 3 per cent that of equivalent gelatin samples which had contained U_3O_8 during the bombardment.

RESULTS

Three separate runs were carried out. In two of these the suspension was neutral and in the third it had been made approximately 0·03N in HNO_3. All these experiments gave essentially identical results and can thus be considered together.

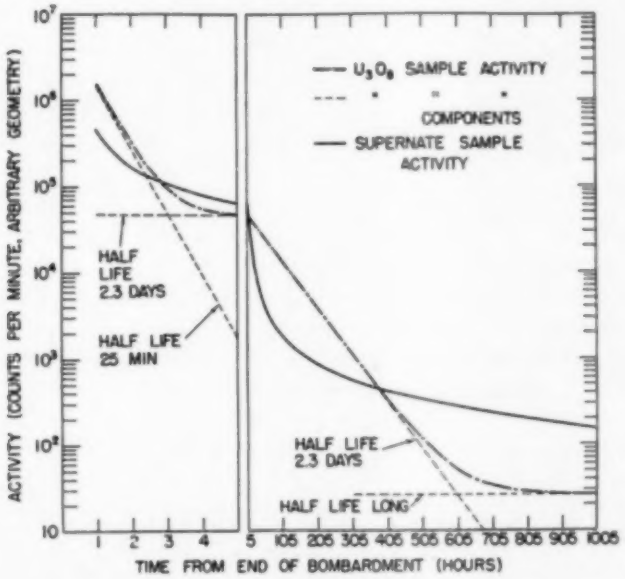

FIG. 1.—Decay of activity in supernate and uranium oxide fractions.

The decay curves of the activity in the supernate and of the activity remaining in the U_3O_8 are given in Fig. 1. The uranium oxide shows 25-min U^{239} activity decaying cleanly into its 2·3-day Np^{239} daughter. The decay of the Np^{239} can then be followed for over fifteen half-lives before it finally dies out, leaving only a small amount of long-lived activity (apparently UX_1 and UX_2 in secular equilibrium with U^{238}). No contribution of fission products to the decay of these samples was detected. On the other hand, the decay of the supernate fractions is typical for gross fission products. As can be seen from Fig. 2, the function

$$A = Ct^{-1\cdot16}$$

(where A is activity, C a constant, and t time) is approximately followed.

These results are exactly what would be expected if all the fission fragments left the uranium phase and entered and remained in the aqueous phase; while the U^{239} and Np^{239} with the much smaller recoil energy imparted them by gamma and beta emission remained in the uranium particles. By comparing the maximum amount of fission

product activity that could have been present in the uranium samples with the fission fragment activity of the supernate fractions, it can be concluded that a separation of at least 99 per cent of the fission product from the uranium particles has been effected.

The fact that the fission fragments left the uranium particles is not surprising: it could hardly have been otherwise, in view of the known data on the recoil energy. It is more remarkable that the fission fragments remained separated, instead of becoming adsorbed on the surface of the uranium oxide particles. This was the true test of the practicability of this recoil method of separation.

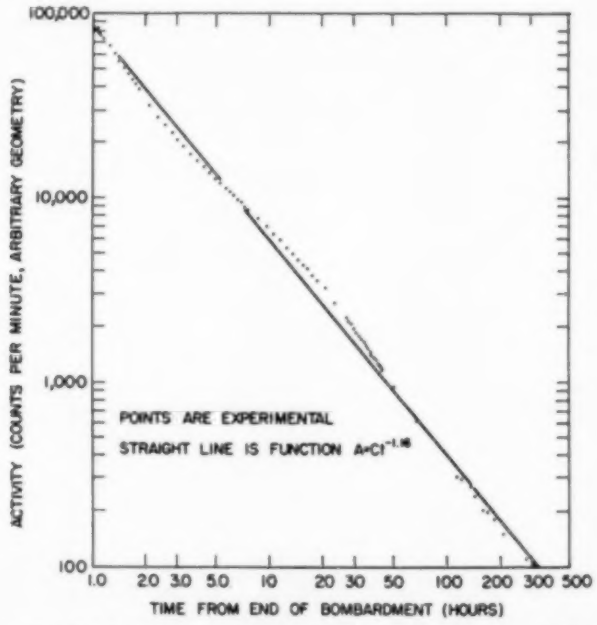
100,000
10,000
1,000
100
ACTIVITY (COUNTS PER MINUTE, ARBITRARY GEOMETRY)
POINTS ARE EXPERIMENTAL
STRAIGHT LINE IS FUNCTION A=Ct^-1.18
1.0 2.0 3.0 5.0 10 20 30 50 100 200 300 500
TIME FROM END OF BOMBARDMENT (HOURS)

FIG. 2.—Log-log plot of decay of fission products in supernate fraction.

This experiment has demonstrated that, by making use of fission-product recoil, pure actinide activities such as Np^{239} and carrier-free gross fission products can be prepared with great ease. While this technique will be useful in the laboratory preparation of such materials, its application to reactor design may be much more important. Reactors may be fuelled with a dispersion of gaseous, liquid, or solid fissile material in a liquid or solid matrix. Such a system would automatically and continuously separate its fission products from the fissile into the other phase. Complex chemical processing is eliminated, and only a simple mechanical procedure such as filtration and centrifugation would be required to complete the elimination of the fision products.[4] Furthermore, the separated fission products are in a concentrated carrier-free form, suitable for disposal or for use as radiation sources.

Acknowledgement—The author gratefully acknowledges the help and advice of MORRIS SLAVIN of this laboratory.

[4] In the case of a solid in solid suspension it may be convenient to use a simple chemical solution procedure to dissolve one of the two phases of the mixture.

Note added in proof—At the International Conference on the Peaceful Uses of Atomic Energy, a Netherlands group (H. DE BRUYN *et al.*, A/CONF. 8/P/936) disclosed that irradiation of a suspension of fine UO_2 in pure water caused several fission products (Ba, Mo, Cs, and I) to appear at least partially in the aqueous phase. It is particularly interesting that readsorption of fission product on the surface of the fuel particles was observed, while in the work reported in this paper, this did not occur. This suggests that the gelatin used in the present work efficiently sequestered the fission products, and thus prevented their readsorption. Undoubtedly, a large number of substances could be used as complexing agents, instead of the gelatin, and would also ensure complete separation.

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J. Inorganic and Nuclear Chemistry, 1956, Vol. 2, pp. 184–191. Pergamon Press Ltd., London

ISOTOPE EFFECTS IN RADIATIVE THERMAL NEUTRON CAPTURE

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(*Received 6 October* 1955)

Abstract—The products of radiative thermal neutron capture in triphenylstibine have been separated by chromatography and identified by specific activity measurements. The radioactive antimony has been found in the form of the parent compound, phenylstibine and diphenylstibine oxides, the corresponding stibonic acids, as well as elementary antimony. These products account for about 80 per cent of the radioactive antimony.

The various products contain different proportions of the Sb^{122} and Sb^{124} isotopes, and their ratios vary from $1{\cdot}37 \pm 0{\cdot}02$ in triphenylstibine to $0{\cdot}88 \pm 0{\cdot}01$ for the elementary antimony.

VERY few investigations have been concerned with the influence of recoil energy and isotope effects on the yields of the products resulting from radiative thermal neutron capture. Different retentions for the two Br^{80} isotopes in neutron-irradiated bromobenzene, bromoform, and the propyl bromides were first reported by CAPRON and co-workers, who ascribed this to differences in the recoil energy of the two isomers.[1, 2, 3,] On the other hand, FOX and LIBBY[4] and ROWLAND and LIBBY[5] found that the retentions of the two isomers were identical in highly purified liquid propyl bromides, and suggested that the separations observed by the previous workers might be due to impurities. They pointed out that if impurities were present which could react with separated bromine to form organic molecules, because of its longer lifetime in solution, the apparent organic yield of the 4·4-hour isomer relative to that of the 18-minute isomer would be increased.

This was confirmed by CHIEN and WILLARD,[6] who concluded that isotope and neutron energy effects were not important in determining the organic yield of bromine in pure liquid alkyl bromides, although apparent isomer effects due to the reaction of products of the Szilard-Chalmers reaction with impurities could easily be observed.

Evidence of a definite isotope effect, manifest as a higher organic yield of Br^{82} relative to $^{\bullet}Br^{80m}$ from neutron-irradiated crystalline organic bromides, has been obtained by LIBBY.[5] This effect was absent in the liquid state, in carbon tetrabromide, and in frozen glasses. Other data also suggest that isotope effects can be obtained when crystalline substances are irradiated. MADDOCK[7] has reported such an effect in crystalline sodium chloro-iridate.

When only a single radioactive isotope is produced by neutron irradiation, the yield of the products containing this isotope may depend upon the energy of the incident neutrons. Such a dependence would suggest that the recoil energy plays a part in determining the yield of the products of the Szilard-Chalmers reaction.

[1] P. C. CAPRON and E. CREVECOEUR *J. chim. phys.* **49**, 29 (1952).
[2] P. C. CAPRON and A. J. VERHOEVE-STOKKINK *Phys. Rev.* **81**, 336 (1951).
[3] P. C. CAPRON and L. J. GILLY *J. chim. phys.* **52**, 505 (1955).
[4] M. S. FOX and W. F. LIBBY *J. Chem. Phys.* **20**, 487 (1952).
[5] F. S. ROWLAND and W. F. LIBBY *J. Chem. Phys.* **21**, 1495 (1953).
[6] J. C. W. CHIEN and J. E. WILLARD *J. Amer. Chem. Soc.* **76**, 4735 (1954).
[7] U. CROATTO, G. GIACOMELLO, and A. G. MADDOCK *Ric. Sci.* **22**, 265 (1952).

BRODA[8] has reported that the yield of radioactive As(V) obtained from irradiated arsenites and arsenates in the solid state depended on the energy of the incident neutrons, while the yield from irradiated solutions was independent of pH, concentration, and temperature.

On the other hand, the yield of radioactive Mn(IV) obtained from irradiated potassium permanganate[9] in the solid state or in solution was independent of the neutron energy. The yield from irradiated solutions depended on concentration and pH. On the basis of this evidence BRODA concluded that the oxidation state of the liberated arsenic was determined in the recoil process, and therefore depended on the recoil energy, while the fate of the liberated manganese was determined by subsequent reactions with water.

Secondary chemical reactions may thus completely obscure any effect brought about by differences in recoil energy, and effects of this nature are likely to be particularly important in the oxy-anions.[10, 11] Such chemical reactions are less likely to affect the distribution of the primary recoil products resulting from the Szilard-Chalmers reaction in organo-metallic compounds.

In a previous communication, preliminary results for the separation of antimony isotopes in crystalline triphenylstibine were reported.[12] Additional results have been accumulated and are reported in this paper. Chromatographic methods were used to separate the products of radiative thermal neutron capture in triphenylstibine and the various fractions examined for isotope separations. The existence of an isotope effect has been substantiated, and the results are compared with those previously obtained for triphenylarsine.

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EXPERIMENTAL

Materials

Triphenylstibine was prepared from antimony trichloride, bromobenzene, and magnesium by a Grignard reaction.[13] The product was purified by repeated recrystallization from petrol ether.

The following compounds were synthesized by the methods described in the references: diphenylstibine oxide,[14] phenylstibine oxide,[15] diphenylstibonic acid,[16] phenylstibonic acid,[17] diphenylpicrylhydrazyl (DPPH).[18]

Irradiations

0·5-g quantities of triphenylstibine were sealed in silica ampoules *in vacuo* for irradiation at Harwell. All the samples were irradiated for one week in the thermal column of BEPO at a flux of approximately 10^{12} neutrons/cm^2 sec.

Analysis of the Irradiated Samples

Amounts of the irradiated samples sufficient to give total activities of the order of 10^6 counts/min were dissolved in 1 ml of AR benzene on top of an alumina column 10 cm × 0·8 cm. Neutral alumina was used for the primary separations, and all analyses were performed in duplicate.

[8] H. MULLER and E. BRODA *Monatsh. Chem.* **82**, 48 (1951).
[9] E. BRODA and W. J. RIEDER *J. Chem. Soc.* **574**, 5356 (1949).
[10] K. J. MCCALLUM and A. G. MADDOCK *Trans. Faraday Soc.* **49**, 1150 (1953).
[11] J. H. GREEN, G. HARBOTTLE, and A. G. MADDOCK *Trans. Faraday Soc.* **49**, 1150 (1953).
[12] N. SUTIN and A. G. MADDOCK *Trans. Faraday Soc.* **51**, 184 (1955).
[13] G. T. MORGAN and F. M. G. MICKLETHWAIT *Trans. Chem. Soc.* **99**, 2290 (1911).
[14] H. SCHMIDT *Ann.* **421**, 236 (1920).
[15] *Ibid.*, 217.
[16] *Ibid.*, 235.
[17] *Ibid.*, 188.
[18] S. GOLDSCHMIDT and K. RENN *Ber.* **55**, 628 (1922).

The chromatogram was developed with 100 ml benzene and then, successively, 100 ml each of 1 per cent alcohol + benzene, absolute alcohol, 10 per cent water + alcohol, water, then 150 ml of 10 per cent acetic acid, 50 ml water, 150 ml 0·1 per cent sodium hydroxide, 50 ml 2N sodium hydroxide, and 100 ml of 5 per cent tartaric + nitric acid. The alumina was finally extruded into sodium hydroxide and its activity and that of the washings measured.

Fractions were collected on a rotating-table automatic collector after passage through a type-F10 flow counter. Activities were measured by a type-1114D ratemeter, the output of which was connected to an Elliot recording milliammeter. When more accurate measurements were required, the fractions were counted, using a type-M6 annular liquid counter.

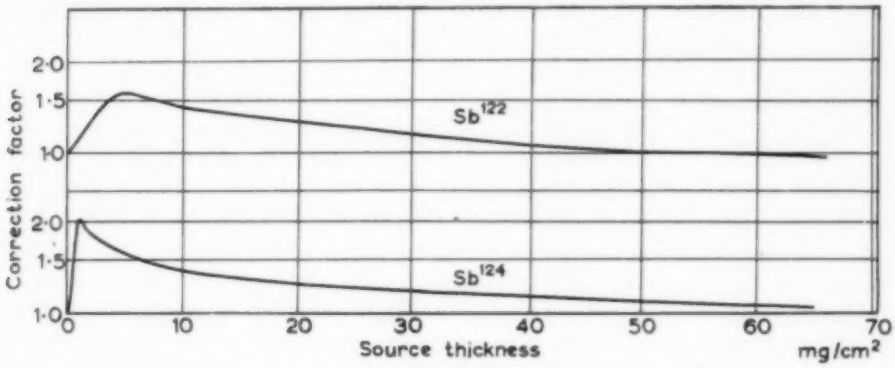

FIG. 1.—Self-absorption corrections for Sb^{122} and Sb^{124} in $SbPh_3$.

Identification of Products

The ultra-violet absorption spectra of the synthesized carriers were measured on a Unicam SP500 spectrophotometer. Readings were taken in the 0·2 to 0·8 optical density ranges, and the solvents were 95 per cent alcohol for the stibine oxides and 1N HCl for the stibonic acids.

Analogies with the products from triphenylarsine suggested carriers to be added to the various eluates, which were then rechromatographed and the specific activities of the fractions from the second chromatogram measured. Any separation of the activity from the added carrier showed up as a variation in the specific activities of the fractions from the second chromatogram. For the specific activities of eluates containing benzene, the eluting agent was removed under reduced pressure and 95 per cent alcohol used as solvent. 5-ml portions of the solution were counted for eight to ten minutes until sufficient accuracy was reached, and the concentration of carrier obtained by measuring the extinction at the appropriate maximum in the ultra-violet.

Measurement of the Sb^{122}/Sb^{124} Ratios

The various fractions were evaporated to dryness in planchettes to give "weightless" sources, and their activities measured with an end-window Geiger counter over a period of thirty days. The proportions of Sb^{122} and Sb^{124} in the various fractions were then determined from the decay curves.

In other runs, sources of thicknesses approximately 50 mg/cm² were prepared by adding appropriate carriers to the various fractions. Self-absorption factors were determined for both isotopes. Several grams of irradiated $SbPh_3$ were purified by chromatography on Grade 1 alumina, followed by extraction of the benzene eluate with sodium hydroxide and acetic acid. Triphenylstibine, which had been allowed to stand for several weeks after irradiation, was used to prepare sources of constant specific activity but varying in thickness up to 100 mg/cm², and the self-absorption corrections for Sb^{124} were determined from these sources. The corrections for Sb^{122} were determined from sources prepared from freshly-irradiated $SbPh_3$. The self-absorption corrections are plotted in Fig. 1.

Due to the large variation in the self-absorption factors in the 0–20 mg/cm² region, figures derived from the "weightless" planchettes were not used in the calculation of the isotope separations. The largest difference in the ratio of the self-absorption factors due to variations in the thicknesses of the

sources was only 7 per cent. Moreover, the orders of the weights of the various fractions were reversed in the different runs. Thus it is unlikely that the isotope separations reported in Table 2 can be accounted for on the basis of self-absorption corrections.

RESULTS

Radiochemical Purity of the Triphenylstibine

Two radioactive isotopes are produced by neutron capture in naturally-occurring antimony:
(1) 2·8-day Sb^{122}, which emits β-rays of 1·36 and 1·94 MeV max. energy and a 0·57-MeV γ-ray.
(2) 60-day Sb^{124}, which emits β-rays of 0·68 and 2·37 MeV max. energy and 1·70 MeV γ-ray.
The radiochemical purity of the samples was established by following the decay of the irradiated crystals for more than sixty days.

Analysis of the Irradiated Samples

The percentages of the total activity of four irradiated samples eluted from neutral alumina by the various solvents are recorded in Table 1. Elution was commenced about forty hours after dissolving the irradiated crystals in benzene. The results of a typical chromatogram are plotted in Fig. 2.

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TABLE 1.—PERCENTAGE OF TOTAL ACTIVITY ELUTED BY THE VARIOUS SOLVENTS

Eluting Agent	Percentage of total Sb^{122} activity			
Benzene	17·5	18·7	10·0	9·0
Sodium hydroxide extraction	2·0	9·2	5·9	12·5
1 per cent alcohol + benzene	1·3	1·2	1·0	1·3
Absolute alcohol	4·0	2·4	3·6	3·9
10 per cent water + alcohol	0·5	1·3	1·3	2·1
Distilled water	1·8	1·6	1·2	4·2
Acetic acid	9·2	9·0	13·0	11·9
0·1 per cent sodium hydroxide	39·1	27·2	35·5	23·8
Tartaric + nitric acid	24·6*	29·4	28·5	31·3

* Does not include alumina washings.

Appreciable amounts of activity could be extracted from the benzene eluate by sodium hydroxide, and this suggested the presence of a labile species. The peak in the activity eluted by alcohol + benzene appeared after 20 ml, while the activity eluted by alcohol, water + alcohol mixture, and water, appeared in the first few fractions of the new eluate. A band was eluted after 15 ml of acetic acid and a broad band after 30–35 ml of 0·1 per cent sodium hydroxide. The tail of this band was eluted by 0·5N sodium hydroxide. The sum of the activity eluted by sodium hydroxide and that extractable from the benzene eluate was approximately constant for all the samples. The activity eluted by concentrated nitric acid presumably corresponds to the liberated antimony. Further activity was generally recovered by washing the extruded alumina, and this has been included in the nitric acid total.

A benzene eluate, which was collected fifteen minutes after dissolving the irradiated crystals, was rechromatographed after it had stood for two days. Several bands were obtained, with the sodium hydroxide fraction in greatest yield, and also appreciable amounts of free antimony. In order to eliminate any confusion caused by the presence of colloidal antimony, the chromatograms were subsequently developed forty hours after dissolving the irradiated crystals.

In order to identify the various fractions, appropriate carriers were added, the mixtures rechromatographed, and the specific activities of the fractions from the second chromatogram determined. These measurements confirmed that the benzene eluate contained a number of compounds, and suggested that the alcohol + benzene activity corresponded to $Ph_2SbOSbPh_2$. The

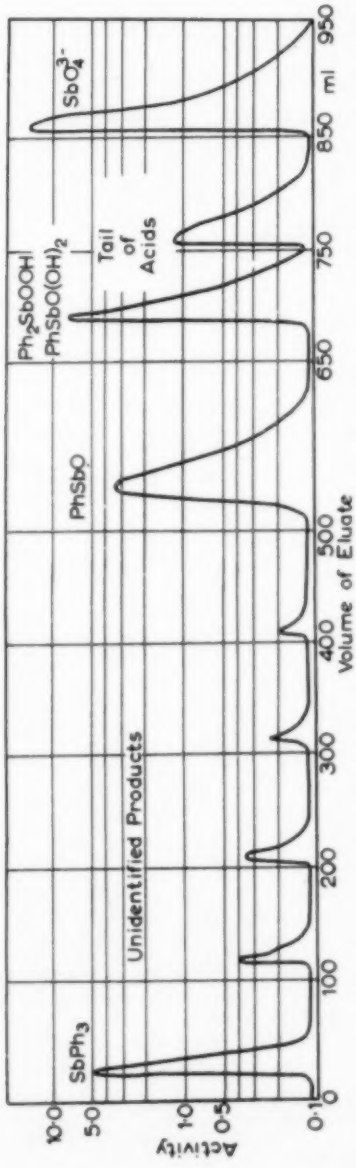

FIG. 2.—Elution chromatogram of irradiated $SbPh_3$.

1–100 ml	benzene	500–650 ml	10 per cent acetic acid
100–200 ml	1 per cent alcohol + benzene	650–750 ml	0·1 per cent NaOH
200–300 ml	absolute alcohol	750–850 ml	2N NaOH
300–400 ml	10 per cent water + alcohol	850–950 ml	5 per cent tartaric + nitric acid
400–500 ml	water		

specific activity measurements also identified the acetic acid activity as PhSbO, and revealed that the sodium hydroxide fraction contained a mixture of stibonic acids.

After 1 mg of diphenylstibine oxide had been added, the benzene eluate was concentrated under reduced pressure and rechromatographed on grade 1 alumina, using benzene and alcohol + benzene mixtures as eluting agents. This separation gave an average of 4·4 per cent for the retention.

The activity eluted by sodium hydroxide was resolved by anion-exchange chromatography. 1 mg each of diphenylstibonic and phenylstibonic acids were added to the 0·1 per cent NaOH eluate; the solution was concentrated, and the pH adjusted to 3·0. Due to changes in the degree of hydration of the stibonic acids, the pH of this solution gradually rose, and had to be readjusted to 3·0. When the pH had remained steady at this value for at least thirty minutes, the solution was chromatographed on the chloride form of Amberlite IR4B ion-exchange resin and eluted with 50 ml water, 100 ml 1N hydrochloric acid, 50 ml water, and 200 ml 2N sodium hydroxide. These ion-exchange separations coupled with specific activity measurements gave an average value of 13·9 per cent for diphenylstibonic acid. It was similarly shown that the sodium hydroxide extract consisted mainly of phenylstibonic acid.

Isotope Separations

The proportions of Sb^{122} and Sb^{124} in the various fractions were calculated from their decay-curves, and the results are recorded in Table 2, together with the results previously reported for $AsPh_2$.[13]

TABLE 2.—ISOTOPE SEPARATIONS

	Sb^{122} (per cent)	Sb^{124} (per cent)	$\frac{Sb^{122}}{Sb^{124}}$	As^{76} (per cent)	$\frac{As^{76}}{Sb^{124}}$
MPh_3	4·4	3·2	1·37 ± 0·02	2·1	0·66 ± 0·15
MPh_2	13·9	13·8	1·01 ± 0·05	12·5	0·91 ± 0·10
MPh	32·7	30·7	1·06 ± 0·04	35·1	1·14 ± 0·15
M	29·7	33·8	0·88 ± 0·01	30·8	0·91 ± 0·04

The ratios obtained for $SbPh_3$ in the various runs are in good agreement, as are those for Sb, while the ratios for the $SbPh_3$ and SbPh derivatives varied for the different samples. The reason for this variation may lie in the 20 per cent of unidentified products, which presumably correspond to compounds in which the radioactive antimony is attached to one or more organic radicals.

Identification of the Recoil Products

Attempts to identify the primary recoil products by reaction with diphenylpicrylhydrazyl did not yield any definite conclusions. Several bands were obtained when the irradiated crystals were dissolved in DPPH solutions and the resulting solutions chromatographed, using petrol ether + benzene mixtures as eluting agents, but these fractions proved too unstable for identification.

DISCUSSION

The products of the Szilard-Chalmers reaction in triphenylstibine are active triphenylstibine, phenylstibine and diphenylstibine oxides, the corresponding stibonic acids, and free antimony. Labile products, which gradually react to give the stibine oxides and stibonic acids, are also produced. By analogy with triphenylarsine, these labiles may correspond to the hydrides, phenylstibine, and diphenylstibine.

The above-named products account for about 80 per cent of the radioactive antimony. The remainder may occur as complex polymeric compounds, or perhaps as products in which the antimony is attached to an aliphatic radical, or to both an

aliphatic and an aromatic radical. Such products could be formed from radicals resulting from the rupture of phenyl rings by the recoiling atom. While the atom is still recoiling with a few hundred eV of energy, it is probable that it loses its energy by breaking bonds in the neighbouring molecules in a rather indiscriminate fashion, giving a whole variety of organic radicals. The results further suggest that, in a substantial part of the slowing-down process, the recoiling atom undergoes inelastic collisions with the triphenylstibine molecule as a whole, rather than with individual atoms. Such inelastic collisions may lead to the rupture of the relatively weak antimony-phenyl bonds by vibrational excitation, and will be most probable when the energy of the recoiling atom has been reduced to the order of 10 eV by collisions. This will lead to a high concentration of free phenyl radicals near the end of the track of the recoiling atom. Once the recoiling atom has been slowed down sufficiently for stable combination to occur, the different products will be formed by the combination of the radioactive atom with the free radicals in its vicinity. In view of the high concentration of phenyl radicals formed near the end of its track, the formation of relatively high yields of products containing antimony-phenyl bonds is not unexpected.

The various products contain different proportions of the two antimony isotopes. Both isotopes have relatively long-lived excited states which decay to the ground state by isomeric transition. 2·8-day Sb^{122} has an isomer with a half-life of 3·5 minutes, while 60-day Sb^{124} has two isomers with half-lives of 21 minutes and 1·3 minutes. These isomers are only formed in about 1 per cent of the neutron captures,[19] but if shorter-lived isomers are formed in appreciable amounts, the observed isotope separations could be accounted for on the basis of differing degrees of bond rupture following internal conversion of the transition energy of the isomers. If the excited states of the isomers are sufficiently long-lived, the isomeric transition would produce further bond rupture in the radioactive recoil products, which might already have reached thermal equilibrium with their surroundings. Alternatively, if the lifetimes of the excited states are relatively short, differing degrees of bond rupture could be produced in the capturing molecules as a result of internal conversion of the softer capture γ-rays. In either case, internal conversion could account for the isotope separations, KAHN[20] however, did not find any isotope separation when irradiating benzene solutions of triphenylstibine, and this would suggest that the isotope separations are not due to internal conversion effects, since it might be expected that these would also be effective in the liquid state. Unfortunately, data on the capture γ-ray spectra of the individual isotopes are not available, but the present results suggest that the recoil energy of Sb^{122} is less than that of Sb^{124}. The smaller the recoil energy, the larger would be the proportion of inelastic collision products, and the smaller the volume in which such radicals would be contained. These factors should lead to a higher retention of the isotope having the smaller recoil energy.

The distributions of the products containing antimony are similar to those containing arsenic produced by the Szilard-Chalmers reaction in triphenylarsine. Triphenylarsine and triphenylstibine both crystallize in triclinic pinacoidal forms; their molar volumes differ by a few per cent, and their melting-points lie within 10°

[19] E. DER MATEOSIAN, M. GOLDHABER, C. O. MUELHAUSE, and M. MCKEOWN *Phys. Rev.* **72**, 1271 (1947).
[20] M. KAHN *J. Amer. Chem. Soc.* **73**, 479 (1951).

of each other. Both molecules have pyramidal structures, though the antimony-carbon bonds are weaker than the corresponding arsenic-carbon bonds.[21] In view of the similar properties of triphenylarsine and triphenylstibine, it seems likely that the quantitative distribution of their products is related to their recoil energies.

The capture γ-ray spectra of arsenic and antimony are summarized below:[22]

	Number of photons in designated MeV energy intervals/100 neutron captures			
	1–3	3–5	5–7	>7
As	~80	47	22	1
Sb	~80	36	12	

Since there is a higher proportion of energetic photons in the arsenic radiation, it is likely that the arsenic atom will have a larger recoil energy than the antimony. The maximum energy available for bond rupture is given by the following relationship:

$$E_R = \frac{536E_\gamma^2}{M}\,\frac{m}{(M+m)}\ \text{eV}$$

where $E\gamma$ = energy of the most energetic photon in MeV.

M = mass of the capturing atom.

m = mass of the remainder of the molecule.

The most energetic photon observed by KINSEY and BARTHOLOMEW[23] in the capture radiation from arsenic has an energy of 7·30 MeV and that from antimony an energy of 6·80 MeV. These values lead to $E_R = 288$ eV for arsenic and 134 eV for antimony, and are consistent with the smaller retention of arsenic in irradiated triphenylarsine.

Other factors which may play an important part are the relative masses of arsenic and antimony and their relative bond energies. Since the mass of an arsenic atom is approximately the same as that of a phenyl group, the recoiling arsenic atom can transfer a larger fraction of its energy in a collision with a phenyl group, and this may compensate for the fact that the arsenic-phenyl bonds are stronger than the corresponding antimony-phenyl bonds.

An investigation of the products of radiative thermal neutron capture in antimony pentaphenyl is in progress, and it is hoped that the results will be of some assistance in interpreting the mechanism of the Szilard-Chalmers reaction in organo-metallic compounds.

Acknowledgements—The authors wish to express their thanks to G. R. MARTIN and Dr. A. G. MADDOCK for many helpful discussions. One of us (N. S.) is indebted to the University of Durham for the award of an Imperial Chemical Industries Fellowship, and the other (R. M. S. H.) to the Ministry of Education for a State Scholarship.

[21] N. V. SIDGWICK, *The Chemical Elements and Their Compounds*, Oxford University Press, 773 (1950).
[22] P. S. MITTELMAN and R. A. LIEDTKE *Nucleonics* **13**, 5, 50 (1955).
[23] G. A. BARTHOLOMEW and B. B. KINSEY *Canad. J. Phys.* **31**, 1025 (1953).

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J. Inorganic and Nuclear Chemistry, 1956, Vol. 2, pp. 192 to 195. Pergamon Press Ltd., London

THE HYDRATES OF ZIRCONIUM TETRAFLUORIDE

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(*Received* 8 *November* 1955)

Abstract—A mono- and a trihydrate of zirconium tetrafluoride have been identified from X-ray diffraction and chemical studies. The monohydrate is body-centred tetragonal with $a = 7{\cdot}70 \pm 0{\cdot}01kX$ and $c = 11{\cdot}63 \pm 0{\cdot}01kX$ and 8 molecules per unit cell. The trihydrate degrades to the monohydrate at 100°C in air, and at room temperature *in vacuo*. The monohydrate when heated in air at 250°C degrades to the oxide and/or oxyfluoride, and *in vacuo* decomposes to an unidentified substance.

INTRODUCTION

CHAUVENET,[1] in 1920, reported the existence of a mono- and a trihydrate of zirconium tetrafluoride, and also the effect of heating these hydrates in air. From an optical crystallographic study, MARIGNAC[2] concluded that the trihydrate was triclinic. No X-ray diffraction studies have, so far, been reported for these hydrates. We have therefore reinvestigated the zirconium tetrafluoride-water system. Our chemical results substantially agreed with those of CHAUVENET, and our X-ray diffraction studies confirmed the existence of the two hydrates, which are not, however, isostructural with the hydrates of thorium[3] and uranium[4] tetrafluoride.

EXPERIMENTAL

Analysis

(a) The fluorine in the hydrate was estimated by the pyrohydrolytic method. A current of steam was passed over the sample, which was heated to 900–1000°C, and the resulting hydrofluoric acid–water mixture was condensed and titrated with standard alkali. The steam jet was then removed and the residual oxide heated in air and weighed as ZrO_2. The water-content was obtained by difference after determining the zirconium and fluorine as above.

The zirconium-source compounds used in this investigation contained small quantities of hafnium. Thus if the residual oxide, after hydrofluorination, is assumed to be solely ZrO_2, then the F/Zr ratio will be low. In all our analyses we have found low F/Zr ratios (see Table 1).

(b) For the X-ray examination of the hydrates we used a Guinier-type focusing camera[5] and monochromatized and focused Cu$K\alpha$ radiation from a bent quartz crystal. To avoid shrinkage errors in the measurement of the Bragg angle θ, a 0·1-mm scale was photographed on to the film before processing. X-ray diffraction photographs of the mono- and the trihydrate are reproduced in Figs. 1 and 2 respectively.

(c) A Vickers projection microscope was employed for the photomicrographic studies. The photomicrographs (×1000) indicate the homogeneity, particle size,

[1] E. CHAUVENET, *Ann. Chim. Phys.* **13**, 59 (1920).
[2] J. C. G. DE MARIGNAC, *ibid.* **60**, 257 (1860).
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FIG. 1.—Zirconium tetrafluoride monohydrate.

FIG. 2—Zirconium tetrafluoride trihydrate.

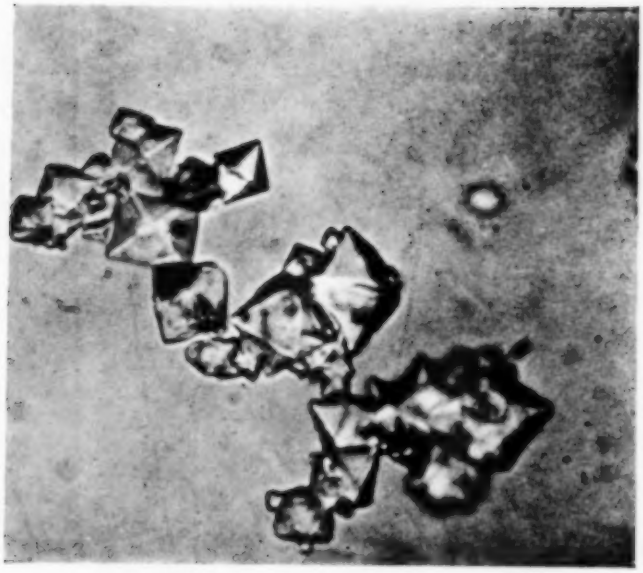

FIG. 3—Zirconium tetrafluoride monohydrate.

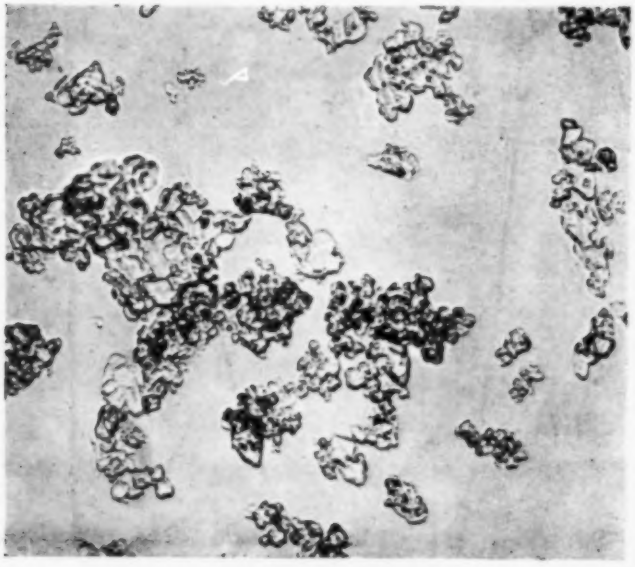

FIG. 4.—Zirconium tetrafluoride trihydrate.

and morphological characteristics of the hydrates. Photomicrographs of the mono- and the trihydrate are shown in Figs. 3 and 4 respectively.

(d) The application of thermogravimetric techniques to phase determination in a two-component system was discussed in a recent paper on the hydrates of thorium tetrafluoride.[3] The same techniques were used in the present investigation.

TABLE 1.—HEATING IN AIR

Initial material	Heat treatment	Analysis of end product	
		*Chemical**	*X-ray*
Trihydrate 1 : 3·93 : 2·94*	100°C	1 : 3·86 : 1·17	Monohydrate
Monohydrate	140°	1 : 3·86 : 1·10	Monohydrate
Monohydrate	200°	1 : 3·90 : 1·00	Monohydrate
Monohydrate	300°	1 : 3·72 : 0·75	Monohydrate plus unidentified phase
Monohydrate	400°	1 : 1·23 : 1·23	$ZrOF_2$ and ZrO_2
Monohydrate	500°		ZrO_2
	HEATING IN VACUO		
Trihydrate	Room temperature	1 : 3·89 : 1·12	Monohydrate
Monohydrate	130°	1 : 3·89 : 1·03	Monohydrate
Monohydrate	170°	1 : 3·89 : 1·03	Monohydrate
Monohydrate	200°	1 : 3·66 : 0·63	Monohydrate plus unidentified phase
Monohydrate	250°	1 : 3·52 : 0·41	Monohydrate plus unidentified phase
Monohydrate	300°	1 : 3·40 : 0·34	Unidentified phase

*Zr : F : H_2O ratio

PREPARATION

(a) *The trihydrate*—Twice the theoretical quantity of 40% aqueous hydrofluoric acid was added to freshly precipitated and dried zirconium hydroxide in a platinum basin. After standing for some time, the insoluble residue was centrifuged off and the resulting solution evaporated to dryness, yielding the trihydrate. Chemical and X-ray diffraction analysis showed the sample to be free from monohydrate.

Another method used for preparing the trihydrate is the addition of about 90% of the theoretical quantity of 40% w/w aqueous hydrofluoric acid to solid zirconium oxychloride. The residual oxychloride, being more soluble than the tetrafluoride hydrate, goes into solution. Thus after centrifuging and washing, with very dilute hydrofluoric acid, the hydrate precipitate is virtually free from contaminating oxychloride. HEVESY and WAGNER[6] suggest that zirconium tetrafluoride trihydrate reacts with aqueous hydrofluoric acid, forming the soluble complex $H_2ZrF_6 \cdot xH_2O$. This reaction would account for our trihydrate yields being low when excess hydrofluoric acid was used in the preparation. The trihydrate prepared by this method was found to contain appreciable quantities of the monohydrate.

[6] G. HEVESY and O. H. WAGNER, *Z. Anorg. Chem.*, **191**, 194 (1930).

(b) *The monohydrate*—This hydrate is formed when the trihydrate, prepared by the second method described above, is washed with acetone and dried by standing in air or dried by standing *in vacuo*.

RESULTS AND DISCUSSION

The monohydrate when dried by washing with acetone or by standing *in vacuo* had a H_2O/ZrF_4 ratio greater than unity (see Table 1). On volume considerations it is unlikely that there is more than one water molecule per metal atom. We also found that the cell constants did not vary with water-content over the range $ZrF_4 . 1{\cdot}0H_2O \rightarrow ZrF_4 . 1{\cdot}2H_2O$. As there was no X-ray crystallographic evidence for the monohydrate's existence over a non-stoichiometric range, we concluded that the excess water is present as adsorbed surface water.

The results of heating the hydrates, contained in platinum vessels, to constant weight in air and *in vacuo*, are shown in Table 1. The trihydrate degrades to the monohydrate when heated at 100°C. According to CHAUVENET,[1] the monohydrate decomposes at 180°C in air, forming the oxyfluoride. However, we observe that the monohydrate is stable up to 250°C.

The trihydrate degrades slowly to the monohydrate when pumped at 10^{-5} mm at room temperature. When the monohydrate is heated above 170° *in vacuo* it starts to decompose, forming an unidentified substance (see Table 1). Our thermogravimetric experiments are in agreement with these latter results.

The thorium tetrafluoride hydrates[3] degraded at 400°C *in vacuo* to the monoclinic anhydrous fluoride and at 300° to a phase which was either a metastable form of the tetrafluoride or a hydrate of exceptionally low water-content.[7] However, as is shown by the results given above, a similar degradation process does not occur with the zirconium tetrafluoride hydrates.

X-ray Diffraction Results

(a) *Monohydrate*—The observed values of $\sin^2\theta$ were found to fit the quadratic form $\sin^2\theta_{hkl} = 0{\cdot}00998\,(h^2 + k^2) + 0{\cdot}00438l^2$, which corresponds to a tetragonal cell with $a = 7{\cdot}70 \pm 0{\cdot}01kX$ and $c = 11{\cdot}63 \pm 0{\cdot}01kX$. The agreement between

TABLE 2.

I_o	$\sin^2\theta_{obs}$	$\sin^2\theta_{calc}$	*hkl*	I_o	$\sin^2\theta_{obs}$	$\sin^2\theta_{calc}$	*hkl*
s	0·0144	0·0144	101	vw	0·1193	0·1195	105
s	0·0375	0·0375	112	w+	0·1344	0·1341	321
w	0·0400	0·0399	200	m	0·1594	0·1597, 0·1594	400, 215
m	0·0493	0·0494	103	s	0·1700	0·1699	314
s	0·0544	0·0543	211	w	0·1745	0·1741	411
m	0·0576	0·0574	202	w+	0·1776	0·1777, 0·1772	116, 402
vvw	0·0700	0·0701	004	m	0·1974	0·1976, 0·1971	206, 332
vvw	0·0800	0·0798	220	w	0·1999	0·1996	420
m	0·0894	0·0893	213	w−	0·2095	0·2091	413
vvw	0·1000	0·0998	310	vw	0·2176	0·2171	422
w	0·1173	0·1173	312				

[7] R. W. M. D'EYE, G. W. BOOTH, E. A. HARPER, A.E.R.E. C/R 1735 (1955).

the calculated and observed values of $\sin^2\theta$ is seen from Table 2 to be good. The density calculated on the basis of 8 molecules per unit cell is 3·54 g/cc, which is in fair agreement with the experimental density of 3·30 g/cc.

The observed indices of the reflections show the following relationships.

$$hkl \text{ present only when } h + k + l = 2n$$

$$hhl \text{ present only when } \quad 2h + l = 4n$$

where n is an integer.

These extinctions are compatible with the space groups $C_{4v}^{11} - I4_1md$ and $D_{2d}^{12} - I\bar{4}2d$. For the latter space-group the special positions 4(a)(b) and 8(c) require the further extinction hkl present only when $2k + l = 2n + l$ or $4n$. As we do not find this extinction, then the zirconium atoms must be placed on the 8(d) special position, and the fluorine atoms on the 8(d) special and/or 16(c) general positions. Similarly in the other space group the same extinction precludes zirconium atoms being placed on the 4(a) special position. The number of variable parameters makes it difficult to determine the atomic positions, but work on this problem is being continued.

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Zirconium tetrafluoride monohydrate is not isostructural with the hydrates of thorium or uranium. CHAUVENET[1] suggested that the monohydrate was an acid zirconyl fluoride $ZrOF_2 . 2HF$. The proof of the correct formulation of this compound must, however, await the results of a complete structural study.

(b) *Trihydrate*—We have so far not succeeded in indexing the complex X-ray diffraction pattern of the trihydrate. The observed intensities and $\sin^2\theta$ values for this hydrate are given in Table 3.

TABLE 3.

I_o	$\sin^2\theta_o$	I_o	$\sin^2\theta_o$
w	0·0114	vw	0·0470
w	0·0128	m	0·0497
s	0·0164	vvw	0·0505
s	0·0204	vw	0·0533
s	0·0234	vw	0·0547
s	0·0254	vw	0·0573
m+	0·0262	w	0·0603
m+	0·0321	vw	0·0624
w	0·0375	vvw	0·0654
s	0·0453	m−	0·0683

Acknowledgements—The authors are greatly indebted to Mr. H. J. HEDGER of Metallurgy Division, A.E.R.E., for some hydrate preparations and also for advice on preparing the hydrates; to Miss G. W. BOOTH for taking the X-ray photographs; and to Dr. E. WAIT for discussion of the X-ray results.

J. Inorganic and Nuclear Chemistry, 1956, Vol. 2, pp. 196–200. Pergamon Press Ltd., London

A TRACER STUDY OF THE DISTRIBUTION OF IODINE BETWEEN CARBON DISULPHIDE AND AQUEOUS SOLUTIONS[1]

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(*Received* 11 *August* 1955)

Abstract—The distribution of iodine between carbon disulphide and water at 25°C has been studied as a function of concentration between 0·1 and 10^{-4}M, and at pH values of about 7, 5, 3, and 1, using 8-d I^{131} as tracer. Below total iodine concentrations of 0·1M (corresponding to about 2×10^{-4}M in the aqueous phase) experimental values of the distribution coefficient are much lower than values calculated from the equilibrium constants for the known reactions of iodine in water.

1. INTRODUCTION

THE use of radioactive tracers has been extensive in the re-investigation of chemical phenomena which have proved difficult to study by ordinary chemical means. One such phenomenon which appears to lend itself readily to such an approach is the chemical behaviour of iodine in water at low concentrations. Recent studies have confirmed older ideas that iodine exists largely as I_2 in its violet solutions, but forms 1 : 1 molecular complexes with the solvent in its brown solutions.[3] Since water solutions of iodine are brown, the existence of a complex of the type $H_2O \cdot I_2$ is assumed. The complex has been found to dissociate by the reaction

$$H_2O \cdot I_2 \rightleftharpoons H_2OI^+ + I^- \qquad (1)$$

which has an equilibrium constant of $1{\cdot}2 \times 10^{-11}$ at 25°C.[4]
The reaction

$$H_2OI^+ \rightleftharpoons HOI + H^+ \qquad (2)$$

follows. The overall reaction is the hydrolysis of iodine and is generally written

$$H_2O + I_2 \rightleftharpoons HOI + I^- + H^+. \qquad (3)$$

The equilibrium constant for (3) has been determined by several different investigators, using various methods, to be approximately 3×10^{-13} at 25°C.[5–9]

The iodide formed in the hydrolysis then reacts with iodine to give tri-iodide ion. This reaction

$$I_2 + I^- \rightleftharpoons I_3^- \qquad (4)$$

[1] This work was supported in part by the U.S. Atomic Energy Commission. Abstracted from a portion of the thesis submitted by M. L. Good to the Graduate School of the University of Arkansas, Fayetteville, in partial fulfilment of the requirements for the degree of Doctor of Philosophy.
[2] Present address: Chemistry Department, Louisiana State University, Baton Rouge, Louisiana.
[3] R. S. MULLIKEN, *J. Amer. Chem. Soc.* **72**, 600 (1950).
[4] R. P. BELL and E. GELLES, *J. Chem. Soc.* 2734 (1951).
[5] W. C. BRAY and E. L. CONNELLY, *J. Amer. Chem. Soc.* **33**, 1485–7 (1911).
[6] E. ANGELESCU and V. D. POPESCU, *Z. phys. Chem.* **156**, 304–8 (1931).
[7] G. HORIGUCHI and H. HAGISAWA, *Bull. Inst. Phys. Chem. Res.* (*Japan*) **22**, 661–4 (1945).
[8] O. WYSS and F. B. STRANDSKOV, *Arch. Biochem.* **6**, 261 (1945).
[9] T. L. ALLEN and R. M. KEEFER, *J. Amer. Chem. Soc.* **77**, 2957 (1955).

has been found to have an equilibrium constant of $1{\cdot}4 \times 10^{-3}$ at 25°C.[10] One other reaction, namely

$$3\,H_2O + 3\,I_2 \rightleftharpoons 6\,H^+ + 5\,I^- + 10_3^- \quad (5)$$

takes place in aqueous solution, but it has been found to reach equilibrium slowly,[4] while reactions (1), (2), and (4) are quite rapid. Also, the equilibrium constant for (5) is of the order of 10^{-48} at 25°C.[11,12] Thus, in most cases this reaction contributes little to the overall iodine reaction in neutral or acidic solutions.

It appears that in aqueous solutions containing macro amounts of iodine (above 10^{-3}M) reactions (1), (2), (4), and (5) explain adequately the observed phenomena. However, at low iodine concentrations, anomalous results are obtained. For example, KATZIN[13] attempted to determine the equilibrium constant for reaction (1) by spectrophotometric methods. At iodine concentrations varying from 2 to 10×10^{-4}M the smallest value of the constant was calculated to be $0{\cdot}52 \times 10^{-8}$, considerably larger than the Bell and Gelles value of $1{\cdot}2 \times 10^{-11}$. Furthermore, successive dilutions of the same stock iodine solution gave successively larger values of the iodine dissociation equilibrium constant. Similar phenomena were observed by REID and MULLIKEN[14] in dilute solutions of iodine in pure pyridine. Their spectrophotometric studies showed that the ratio $[I_3^-]/[Py \cdot I_2]$ increased at high dilutions rather than diminished, as would be expected.

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Since iodine exists in its violet solutions as the free I_2 molecule, one should be able to study the aqueous reactions of iodine by distributing it between one of these solvents and water. By employing tracer techniques, the lower limit of the concentration range could be extended considerably below that of ordinary chemical methods and somewhat below that of spectrophotometric methods. In an effort to study these iodine reactions as a function of pH and concentration, the distribution of iodine between carbon disulphide and water (buffered to various pH values) has been extensively studied.

2. EXPERIMENTAL

Procedure—The carbon disulphide was pre-treated by a method described by EDWARDS and DAVIES.[15] Ordinary distilled water was redistilled from alkaline permanganate solution. The buffers at pH 6·97, 4·97, and 3·15 were made from 0·1M citric acid and 0·2M disodium phosphate. For a pH of 0·96 a dilute solution of sulphuric acid was used. The pH values were obtained with a Beckman Model G pH meter. C.p. iodine, from a freshly opened bottle, was used to prepare the carrier solutions of iodine in carbon disulphide. All carrier solutions were diluted from a 0·1M stock solution. Eight-day I^{131} obtained from Oak Ridge National Laboratory in a "carrier-free" state in sodium sulphite solution was used as a tracer. The radioactive solutions to be used in the distributions were obtained by shaking 25 ml of a carbon disulphide solution containing carrier iodine with 25 ml of diluted I^{131} solution for approximately two minutes, and separating the two phases. The carbon disulphide then contained iodine carrier, tagged with I^{131}. All radioactivity measurements were made by gamma-counting of liquid samples on a scintillation counter. An RCA-5819 photomultiplier tube was used in conjunction with a thallium-activated sodium iodide crystal immersed in oil. A Nuclear Corporation scaling unit, Model 162, was used as a power supply, discriminating circuit, and scaler.

Distribution studies were made by adding 20 ml of the carbon disulphide solution containing

[10] G. JONES and B. B. KAPLAN, *J. Amer. Chem. Soc.* **50**, 1845–64 (1928).
[11] V. SAMMET, *Z. phys. Chem.* **53**, 665 (1905).
[12] W. O. LUNDBERG, C. S. NESTLING, and J. E. AHLBERG, *J. Amer. Chem. Soc.* **59**, 264 (1937).
[13] L. I. KATZIN, *J. Chem. Phys.* **21**, 490–01 (1953).
[14] C. REID and R. S. MULLIKEN, *J. Amer. Chem. Soc.* **76**, 3869–74 (1954).
[15] R. R. EDWARDS and T. H. DAVIES, *National Nuclear Energy Series*, Book 1, *Radiochemical Studies; The Fission Products*, Paper 23, McGraw-Hill Book Company, Inc., New York (1951).

radioactive iodine to 20 ml of buffered water in a 100-ml round bottom, ground-glass stoppered flask. The flask was attached to a mechanical shaker and immersed in a water-bath controlled at 25 ± 1°C. 1-ml samples of both phases were removed from the reaction flask at intervals, but only the water samples were counted. The total activity of the system was determined by counting 1-ml samples of the carbon disulphide solutions before distribution.

Exchange techniques were employed in an attempt to determine the chemical state of the iodine in the water-layer after a distribution had been made. First 2 ml of a water solution was shaken for approximately 1 min with an equal volume of pure carbon disulphide, and 1-ml samples of each layer counted. Only 4 per cent of the activity back-extracted into the carbon disulphide, indicating the presence of very little I_2 in the water-layer.

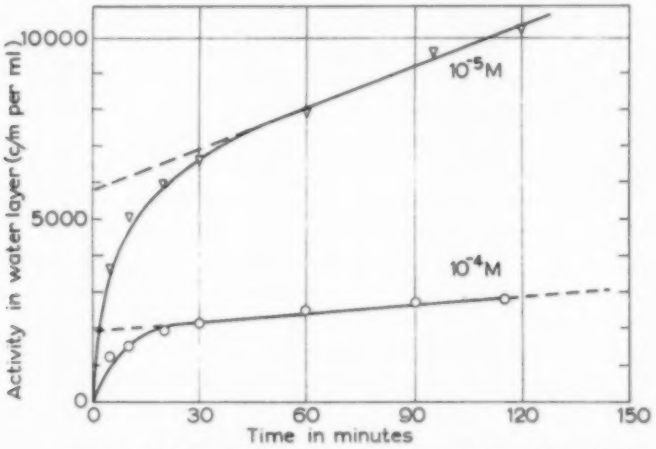

Fig. 1.—Variation of I^{131} activity in water-layer (pH = 4·97) with time (10^{-4}M, and 10^{-5}M iodine in carbon disulphide).

The same procedure was repeated, using 2 ml of carbon disulphide containing 10^{-3}M carrier iodine. Ninety-two per cent of the activity was found in the carbon disulphide, indicating that most of the activity in the water-layer was in a reduced form as I^- or HOI, since these chemical states of iodine are known to exchange quite rapidly with I_2.

3. RESULTS AND DISCUSSION

Plots of activity in the water-layer versus time were made. The activity rose very rapidly at first and then slowly over a long period of time. To obtain the equilibrium values for the fast reaction free from contribution of the following slow one, the straight portion of the curve was extrapolated back to zero time (Fig. 1). Different buffers at approximately the same pH were used in a few runs, but essentially the same results were obtained at a given concentration and pH, regardless of the type of buffer. By repeating several runs, the reproducibility was estimated to be good to 5 per cent.

Distribution coefficients characteristic of the initial rapid transfer of radioactivity were obtained from the relationship

$$D = \frac{(\text{Orig. act. in } CS_2/\text{ml}) - (\text{extrapolated act. in } H_2O/\text{ml})}{(\text{extrapolated act. in } H_2O/\text{ml})}$$

Considering the partition coefficient K_1 calculated to be 568 by Paul[16] from data of Herrero,[17] the hydrolysis constant K_3, and the tri-iodide instability equilibrium

[16] M. A. Paul, *Principles of Chemical Thermodynamics* (McGraw-Hill Book Company, New York), pp. 457, 458 (1951).

[17] G. Herrero, *Physikalisch-Chemische Tabellen*, (*Landolt-Bornstein*), 5th ed., Supplement 111a, p 659 (1935).

constant K_2, an expression for the expected distribution coefficient may be obtained, as shown by KAHN.[18] If D is defined by:

$$D = \frac{\text{activity in } CS_2/\text{ml}}{\text{activity in } H_2O/\text{ml}}$$

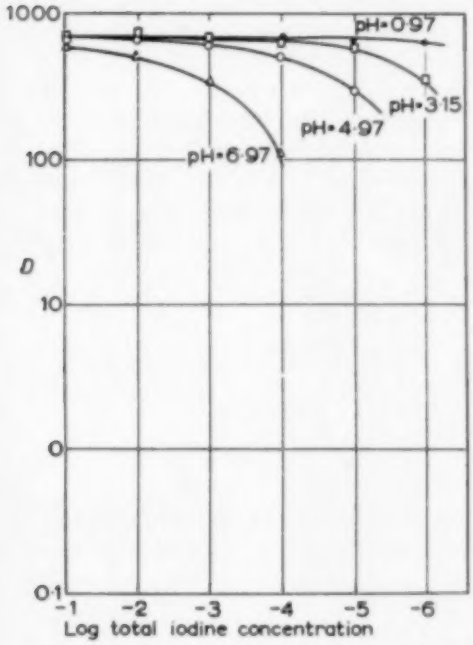

FIG. 2.—Calculated concentration dependence of D.

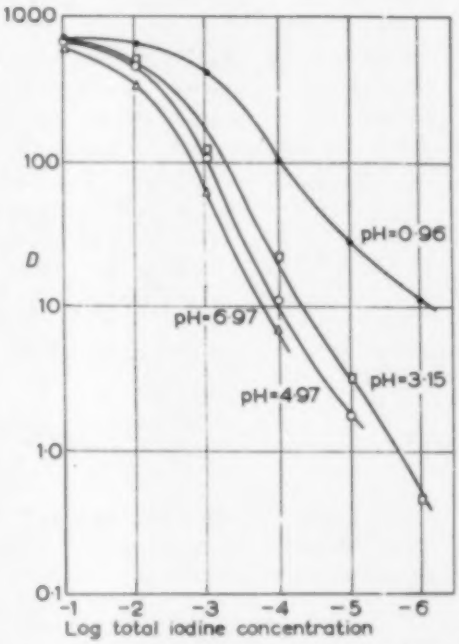

FIG. 3.—Observed concentration dependence of D.

The expected value may be expressed by

$$D = \frac{[I_2]_{CS_2}}{\frac{[I_2]_{CS_2}}{K_1} + \left[1 + \frac{2[I_2]_{CS_2}}{K_1 K_2}\right]\left\{\frac{K_3[I_2]_{CS_2}}{K_1[H^+]\left[\frac{[I_2]_{CS_2}}{K_1 K_2} + 1\right]}\right\}^{\frac{1}{2}}}$$

Thus, D may be calculated for any value of iodine concentration in the carbon disulphide, and the corresponding pH of the aqueous phase. A comparison of the experimental D values with the calculated D values as functions of the total original iodine concentration and the pH of the aqueous phase are shown in Figs. 2 and 3.

At total iodine concentrations of 10^{-1}M the experimental D values agree quite well with the calculated ones at all pH values. Below this concentration, however, the experimental values deviate, the greatest deviation being at the highest dilution. Thus, below total iodine concentrations of 0·1M (approximately 2×10^{-4}M in water) some other phenomenon (or phenomena) apparently contributes more activity to the water-phase than can be accounted for by a combination of the partition function, hydrolysis, and tri-iodide formation.

[18] M. KAHN, Thesis submitted for degree of Doctor of Philosophy, Washington University, St. Louis, Mo. (1950).

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To account for these discrepancies, a reaction (or reactions) must be postulated involving the interaction of the iodine with something in the water-phase (either water itself, the buffering salts, or impurities), causing a disturbance of the well-established equilibria at macro concentrations. Since the type of buffer apparently does not influence the D value markedly, the interaction of iodine with the buffers seems not likely. Considering the specific buffers used, (a) the only common reaction between phosphate and I_2 leads to the production of IO_3^-,[19] and no appreciable amount of IO_3^- was found in the aqueous solutions after distribution; (b) there is no known reaction of iodine and citric acid; and (c) study of the spectra of iodine solutions has led to the conclusion that sulphuric acid acts as an inert solvent for iodine.[20]

Considering an I_2-impurity interaction, as postulated by Katzin,[13] the low D values may be explained by an argument which has been applied to pyridine solutions of iodine.[14] Assuming all of the known rapid and reversible equilibria as being involved, the following would be obtained:

$$I_2(CS_2) \rightleftharpoons I_2(H_2O)$$

$$H_2O + I_2 \rightleftharpoons H_2O \cdot I_2 \rightleftharpoons H_2OI^+ + I^-$$
$$\downarrow\uparrow \qquad +$$
$$HOI \qquad H_2O \cdot I_2$$
$$+ \qquad \downarrow\uparrow$$
$$H^+ \qquad I_3^- + H_2O$$

If an impurity reaction of $H_2O \cdot I_2$ to form I^- becomes important at low concentrations, an excess of I_3^- would be formed. Then at further dilution the I_3^- redissociation would appear as

$$I_3^- + H_2O \rightarrow H_2OI^+ + 2I^-$$
$$\downarrow\uparrow$$
$$HOI + H^+.$$

Thus, the existing equilibria would be upset and excess activity would be found in the aqueous phase. It is difficult to explain, however, why impurity reactions would not give rise to poor reproducibility in a series of experiments.

It is interesting to note that a similar phenomenon was observed by Kahn.[18] In a study of the distribution of I_2 between benzene and water (dilute sulphuric acid at pH 1·3), the D value decreased from 394 at 0·21M total I_2 concentration to 320 at $1{\cdot}9 \times 10^{-4}$M total I_2 concentration. Kahn calculated a value of 395 for D over this range of concentration, considering only the known partition coefficient of I_2 between benzene and water, the hydrolysis of iodine, and the formation of I_3^-. This decrease in D was attributed to a reaction of I_2 with impurities to form benzene-insoluble compounds, or to unknown reactions involving I^- and HOI.

[19] A. Skrabal and J. Gruber, *Monatsh.* **37**, 535–48 (1917).
[20] J. G. Bower and R. L. Scott, *J. Amer. Chem. Soc.* **75**, 3583–5 (1953).

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LETTERS TO THE EDITORS

Isopolyvanadates in Acidic Solution

(*Received* 4 *November* 1955)

THERE is considerable uncertainty as to the nature of the orange-yellow vanadium (V) species which exist in acidic media. The possible occurrence of other cations than VO_2^+ has often been discussed, and the coloured isopolyvanadates have been variously considered to contain from two to ten vanadium atoms. The most commonly accepted formulae for the predominant anion at pH ~ 3 are: $HV_6O_{17}^{3-}$ (DÜLLBERG[1]), $H_4V_8O_{16}^{8-}$ (JANDER and JAHR[2]), and $V_{10}O_{27}^{4-}$ (BRITTON and WELFORD[3]); cf. reference (4) and references therein.

In the present work, solutions containing vanadium (V), hydrogen and sodium ions have been titrated with solutions containing vanadium (V), hydroxyl and sodium ions at 25°C in such a way that the total concentration B of vanadium was held constant in each titration. All solutions were made 1M with respect to perchlorate ions, and the total concentration of vanadium was varied

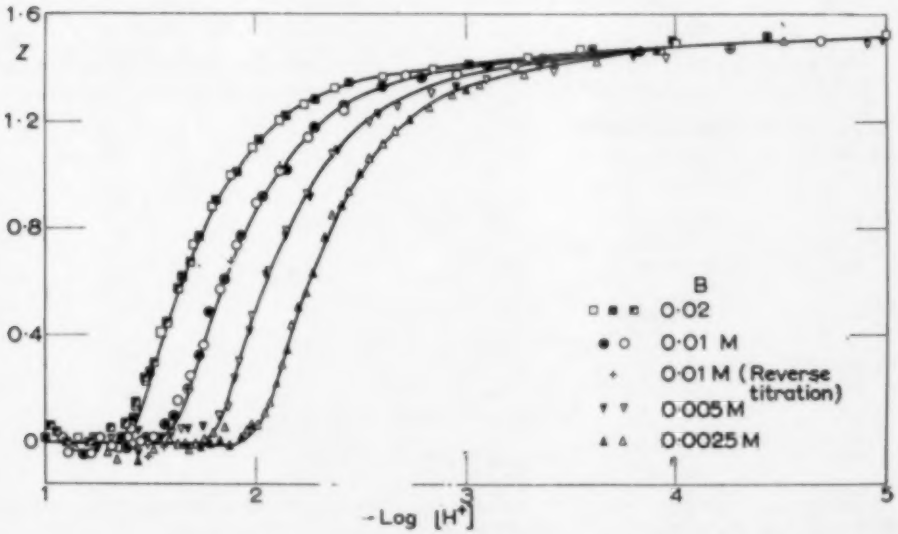

FIG. 1.—The average number of hydroxyl groups Z bound to each VO_2^+ ion as a function of the logarithm of the equilibrium hydrogen-ion concentration [H⁺]. For $10^{-0.5} \geq [H^+] \geq 10^{-7.0}$, $Z \sim 1{\cdot}6$. The symbols represent titration points using total concentrations of vanadium in the range $0{\cdot}02M > B > 0{\cdot}0025M$. The lines represent theoretical formation curves, calculated using the following equilibrium constants: $\log \kappa_{14,10} = -6{\cdot}75$, $\log K_1 = -3{\cdot}6$, $\log K_2 = -5{\cdot}8$.

(1) P. DÜLLBERG, *Z. phys. Chem.* **45**, 129 (1903).
(2) G. JANDER and K. JAHR, *Z. anorg. Chem.* **212**, 1 (1933).
(3) H. T. S. BRITTON and G. WELFORD, *J. Chem. Soc.*, 764 (1940).
(4) J. F. HAZEL, W. M. MCNABB, and R. SANTINI, *J. Phys. Chem.* 57, 681 (1953).

(2×10^{-3}M $\geq B \geq 2{\cdot}5 \times 10^{-3}$M) in different potentiometric titrations. The equilibrium hydrogen-ion concentration ($1 \leq$ pH ≤ 7) was measured using a glass electrode in conjunction with the reference half-cell:

$$\text{Ag/0·01M } AgClO_4 + \text{ 0·99M } NaClO_4\text{/1M } NaClO_4$$

Supplementary spectrophotometric measurements were made in strongly acidic solutions.

The results provide no evidence for the existence of any other cation than VO_2^+, or of anions containing five or six vanadium atoms (cf. refs. 1 and 2). A number of approaches, including the "core + links" treatment,[5] indicate that the two predominant species in the range $1{\cdot}4 \leq$ pH $\leq 2{\cdot}8$ are VO_2^+ and either $[(VO_2)_{10}(OH)_{14}]^{4-}$ or $[(VO_2)_{11}(OH)_{15}]^{4-}$. In all these formulae, two —OH groups cannot be distinguished from one —O— group, so that hydration is uncertain. The data in the range $2{\cdot}8 \leq$ pH $\leq 7{\cdot}0$ may be interpreted in terms of a further hydrolysis of one of these polynuclear complexes, or of the formation of a series of "core + links" complexes of a higher degree of condensation (cf. ref. 5). The accuracy of the present data permits no certain distinction between such hypotheses.

However, recent preliminary crystallographic results support one of these interpretations. LINDQVIST,[6] and EVANS, MROSE, and MARVIN[7] have examined some orange polyvanadates, which crystallize from solutions of pH $\sim 6{\cdot}5$. These salts include: $(NH_4)_6V_{10}O_{28}, 6H_2O$; $K_6V_{10}O_{28}, 9H_2O$; $K_6V_{10}O_{28}, 10H_2O$; $Ca_3V_{10}O_{28}, 16H_2O$; $K_2Mg_2V_{10}O_{28}, 16H_2O$; and $K_2Zn_2V_{10}O_{28}, 16H_2O$. Analytical data are in good agreement with the formulae quoted, and the salts all contain multiples of ten vanadium atoms per unit cell.

Hence, the most probable interpretation of the present data is in terms of the following equilibria:

$$10VO_2^+ + 8H_2O \rightleftharpoons H_2V_{10}O_{28}^{4-} + 14H^+ \qquad \log \kappa_{14,10} = -6{\cdot}75 \pm 0{\cdot}15$$

$$H_2V_{10}O_{28}^{4-} \rightleftharpoons HV_{10}O_{28}^{5-} + H^+ \qquad \log K_1 = -3{\cdot}6 \pm 0{\cdot}3$$

$$HV_{10}O_{28}^{5-} \rightleftharpoons V_{10}O_{28}^{6-} + H^+ \qquad \log K_2 = -5{\cdot}8 \pm 0{\cdot}3$$

A full account of this work, which is part of a programme financially supported by the Swedish Natural Science Research Council, will be submitted for publication in *Acta Chemica Scandinavica*.

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[5] L. G. SILLÉN, *Acta. Chem. Scand.* **8**, 299, 318 (1954).
[6] I. LINDQVIST, private communication.
[7] H. T. EVANS, M. E. MROSE, and R. MARVIN, *Amer. Min.* **40**, 314 (1955).

The Alpha Half-life of Am^{241}

(*Received* 13 *December* 1955)

SEVERAL values have been reported for the alpha half-life of Am^{241}, the most recent being 470^{+5}_{-10} years (HARVEY[1]). By measuring the specific activity of a pure americium sample, we have obtained a new value of $461{\cdot}3 \pm 1{\cdot}7$ years.

A stock solution of americium in nitric acid was prepared. A weighed sample of solution was transferred to a platinum crucible, the solution was evaporated to dryness, and after ignition at 890°C the americium was weighed as AmO_2. A further weighed sample of the stock solution was diluted to 25 ml in a standard flask, and from this 10-μl samples were pipetted with an Agla microburette on to platinum counting-trays. These sources were counted in a low-geometry proportional counter ("new" counter, HURST and HALL[2]) and the counts for replicate sources agreed to within the statistics of counting.

[1] B. G. HARVEY, *Phys. Rev.* **85**, 482 (1952).
[2] R. HURST and G. R. HALL, *Analyst* **77**, 790 (1952).

Three separate determinations of the specific activity were made, and the results are given in Table 1:

TABLE 1.—HALF-LIFE OF Am^{241}

Experiment	Specific activity	Half-life
1	$7{\cdot}146 \times 10^6$ α/min/μg	460·6 ± 0·9 years
2	$7{\cdot}129 \times 10^6$ α/min/μg	461·7 ± 0·9 years
3	$7{\cdot}132 \times 10^6$ α/min/μg	461·5 ± 1·2 years
	Mean value	461·3 years

The purity of the americium was carefully studied, and the only impurity which could be detected was 0·15 ± 0·04% of magnesium. The geometry of the counter was measured to ± 0·15%. This counter is identical with those (counters 12 and 13) used in the comparison-counting experiment with Dr. H. P. ROBINSON, of the Berkeley Laboratory.[3] The errors given for the three separate experiments (Table 1) are computed from all the known sources of error. Two other principal sources of error are (a) the unlikely possibility that there is an undetected impurity present, and (b) the possibility that the americium oxide weighed is not stoichiometric AmO_2. X-ray studies of the final product show that only a single phase is present and that the oxide is isomorphous with ThO_2, UO_2, and PuO_2. The error given for the final result, however, is double the standard error which is calculated from the errors on the individual results in Table 1.

The work summarized in this communication will be described in more detail in a subsequent paper. It is hoped that the present result will then have been confirmed by a further measurement of the americium specific activity, using another compound of more certain composition.

The value for the half-life of Pu^{241} (MACKENZIE *et al.*[4]), which depends directly on that of Am^{241}, is now increased to 13·25 years.

Acknowledgements—The authors wish to thank Mr. F. T. BIRKS for many spectrographic analyses, and Dr. E. WAIT, who examined the X-ray diffraction photographs.

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[3] K. M. GLOVER and G. R. HALL, *Nature* **173**, 991 (1954).
[4] D. R. MACKENZIE, M. LOUNSBURY, and A. W. BOYD, *Phys. Rev.* **90**, 327-328 (1953).

Absence of Rapid Exchange in Solutions of Thiocyanate and Elementary Sulphur

(*Received* 30 *December* 1955)

IT is a well-known fact that the exchange of sulphur between S^{--} and CNS^- is very slow,[1] and it seemed worth investigating whether the same is true for the exchange between S_8 and CNS^-.

Experiments were performed both in ethanol and in acetone. The latter solvent is of special interest as it is used for the reaction between sulphur and cyanide ion,[2] which takes place very rapidly in it.

[1] A. W. ADAMSON and P. S. MAGEE, *J. Amer. Chem. Soc.* **74**, 1590 (1952); G. B. HEISIG and R. HOLT, *J. Amer. Chem. Soc.* **74**, 1597 (1952).
[2] J. K. BARTLETT and D. A. SKOOG, *Anal. Chem.* **26**, 1008 (1954); **27**, 369 (1955).

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Solutions were made of radioactive sulphur (S_8^{35}), 50 mg in 125 ml ethanol or 20 mg in 100 ml acetone. (The radioactive sulphur was obtained either from $BaSO_4$ by reduction *in vacuo* with carbon to BaS, followed by precipitation from a solution as sulphur by means of iodine, or it was sulphur which had been irradiated in the reactor at Kjeller for the production of radiophosphorus. In the latter case aged sulphur was used, and it was recrystallized from CS_2 until the β absorption curve indicated the absence of P^{32}. This sulphur was kindly given to us by the Isotope Laboratory of Philips-Roxane.) Then ten times the equivalent quantity of inactive sulphur was added, as KCNS to ethanol and as NH_4CNS to acetone. The mixture was left to stand at room temperature for the exchange to take place, and at the end of this period the solution was boiled down to a fraction of its previous volume; sulphur was then precipitated by the addition of water. Finally, the sulphur was oxidized by means of nitric acid and isolated as $BaSO_4$.

An inactive solution of sulphur in the organic solvent was added to the liquid to obtain a second sulphur precipitate, intended as a scavenger for elementary sulphur which had remained in solution. In the case of acetone this treatment was repeated, and then the thiocyanate was isolated as AgCNS. The radioactivity was measured on infinitely thick layers by means of a thin-window beta counter, and corrections were applied for the difference in self-absorption in $BaSO_4$ and in AgCNS. In most cases slight activities were encountered in the AgCNS, but as these were very irreproducible, and as they were strongly affected by repeated precipitations of elementary sulphur, it seems probable that they were due mainly to impurities. This assumption is supported by the fact that silver thiocyanate obtained from solutions in acetone similar to those used for normal exchange experiments, but in which the exchange was allowed to go on for only about 5 min, showed activities which corresponded to a very appreciable fraction of those found in the main runs. (Also, solutions in acetone change their colour during the experiments, which suggests the possible formation of radioactive sulphur compounds.)

The highest activities found in the AgCNS amounted to a transfer of $3 \cdot 10^{-3}$ of the elementary sulphur and $3 \cdot 10^{-4}$ of the thiocyanate sulphur during five days with KCNS in ethanol, and to a transfer of 10^{-3} of the elementary sulphur and 10^{-3} of the thiocyanate sulphur during twenty-one days with NH_4CNS in acetone; but, as remarked above, in other cases the activities found in the thiocyanate were much lower.

If we assume that the exchange follows a bimolecular scheme with CNS^- and S_8 as reactants, and if we use the figures given above as upper limits, it can be said that the rate-constant for the exchange process amounts to less than 10^{-6} l/mole-sec. We may add that this upper limit will be valid for any bimolecular mechanism through which the exchange process can take place, either between CNS^- and S_8 rings or between CNS^- and open S_8 chains in equilibrium with rings. If dissociation products take part in the reaction, or if open S_8 chains react with CNS^- before they reach equilibrium with the S_8 rings, the reaction will not follow the bimolecular formula.

This investigation is part of the research programme of the Foundation for Fundamental Research of Matter (F. O. M.). It was carried out with the financial support of the Organization for Pure Scientific Research (Z. W. O.).

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J. Inorg. Nucl. Chem., 1956, Vol. 2 pp. 205 to 208. Pergamon Press Ltd., London

THE THERMAL NEUTRON CAPTURE CROSS-SECTION OF Np^{237}

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(*Received* 5 *December* 1955)

Abstract—A value of 172 ± 7 barns has been obtained for the thermal neutron capture cross-section of the reaction $Np^{237}(n,\gamma)Np^{238}$. The growth of Pu^{238} (the daughter of 2·1-day Np^{238}) in a sample of Np^{237} irradiated in the BEPO pile was measured by α-pulse-height analysis. The neutron flux was obtained by use of gold monitors. The cadmium difference method was used to distinguish the thermal neutron processes from those caused by epi-cadmium neutrons.

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A VALUE of 170 ± 20 barns for the capture cross-section of Np^{237} has been reported.[1] In the present experiments an attempt has been made to reduce the limits of error and to measure the amount of reaction caused by the epi-cadmium neutrons in the BEPO pile.

Foils of Np^{237} (α, 2·20 ± 0·04 × 10^6 yr)[2] were irradiated in BEPO, and the amount of Np^{238} (β, 2·1 days) thus formed was obtained by measurement of its daughter nuclide, Pu^{238} (α, 89·6 ± 0·4 yr).[3] The α-particles from Pu^{238} have an energy of 5·49 MeV, and are thus easily distinguished from those of Np^{237}, 4·77 MeV, by α-pulse-height analysis. The neutron flux received by the Np^{237} was measured by placing gold wires or foils in close proximity. The activity of the gold (Au^{198}, β, 2·70 days) was obtained by dissolving the metal in acid, diluting, and counting aliquots in a 4π-type proportional β-counter.

The contributions from neutrons in the epi-cadmium region (i.e., of energy greater than about 0·4 eV) were obtained by irradiating foils and flux monitors inside cadmium boxes. These were placed a few inches away from the uncovered foils and irradiated at the same time. The contributions from thermal neutrons (energy less than about 0·4 eV) were obtained in the usual manner by subtracting the "cadmium covered" contributions from the "uncovered" contributions.

EXPERIMENTAL

Irradiations

A set of eight Np^{237} sources on thin aluminium disks was prepared. These sources were sufficiently thin and uniform for the energy distribution of the emitted α-particles to be measured in a gridded ion chamber operated in conjunction with a 30-channel pulse-height analyser. The neptunium before irradiation showed a contamination of about 1% of α-activity from Pu^{239} and Am^{241}. The neptunium sources were placed against clean thin aluminium disks ("blanks"), so that the neptunium was sandwiched. The gold-flux monitors were either of weighed gold wire, diameter 0·0127 cm = 0·005 in. wrapped closely around the sandwich, or of weighed gold foils, thickness 0·00052 cm = 10 mg/cm², held against the sandwich by a third thin aluminium disk. Each assembly was wrapped in thin aluminium foil, thickness 0·0007 cm = 1·8 mg/cm². These assemblies could be placed inside small flat cadmium boxes of wall-thickness approximately 0·1 cm = 0·040 in.

In making cadmium difference measurements it is important that the covered and uncovered

[1] Compilation of Neutron Cross Sections, A.E.C.U. 2040, supplement 2, June 1953.
[2] S. FRIED, private communication.
[3] A. H. JAFFEY and J. LERNER, ANL 4411.

samples be irradiated in positions of identical neutron flux. However, the covered and uncovered samples cannot be placed very close together, for the cadmium boxes cause a depression of the thermal flux which extends several centimetres outside the box. In the first two irradiations the covered and uncovered assemblies were placed at either end of a 12-in.-long aluminium can, the central portion of which was filled by a graphite cylinder. These cans were turned end for end twice during the 2·5-day irradiation in an attempt to ensure that both ends were exposed to the same flux. This method proved troublesome, and was abandoned in the last two irradiations, in which the covered and uncovered assemblies were at either end of a 3-in.-long aluminium can packed with silica wool and irradiated without turning for 2 days.

The gold wire of 0·0127-cm diameter has a significant self-shielding for neutrons, and a correction of 4·6% had to be applied.[4] The self-shielding of the gold foil, thickness 0·00052 cm, can be neglected for the present purpose.

Determination of Pu^{238} formed

The irradiated sources were allowed to stand for at least 20 days (10 half-lives for Np^{238}) before α-pulse analysis. The ratio of the α counts in the peaks corresponding to Np^{237} and Pu^{238} was obtained after a small correction for the amount of Am^{241} present before irradiation (Pu^{238} and Am^{241} have almost identical α energies). Because of the short half-life of Pu^{238} (89·6 yr) compared with Np^{237} ($2{\cdot}20 \times 10^6$ yr), irradiations of a few days in a flux of 10^{13} neutrons/cm² sec are sufficient to give a Pu^{238} activity about equal to that of the Np^{237}. The amount of Np^{237} actually destroyed during such an irradiation is negligible.

The "blanks" which had covered the sources during irradiation were also α-analysed. Some α activity (in greatly varying amount) had been transferred to them. Each "blank" showed the same α distribution as its corresponding source, and so it would appear that the transfer was mechanical and not brought about by any recoil process. As only the ratio of Pu^{238}/Np^{237} is required, this transfer is of no consequence.

Determination of flux

The gold was dissolved in a little aqua regia and the solution diluted to known volume. Gold-carrier was used where necessary to ensure that the final gold concentration was about 10 μg/ml. Aliquots of 50·07 microlitres, measured by a calibrated micropipette, were used for counting on 250 μg/cm² aluminium films. The counter was a conventional 4π type, methane flow, proportional β-counter. A paralysis of 5 μsec was imposed in the scaling circuit, and this "dead time" was used to correct the observed counting-rates. Initial counting-rates were between 500 and 8000 counts/sec, and the decay of the sources was followed down to rates in the order of 100 counts/sec. The corrected counts showed no significant deviation from a half-life of 2·70 days, indicating that "dead-time" losses were not significantly different from those computed on the basis of 5 μsec. In each case several sources were prepared, the deviations between them being not more than ±0·5% from the mean.

The 250-μg/cm² aluminium films cause a loss of β-counts. The necessary correction, which can be estimated with sufficient accuracy from the work of PATE and YAFFE,[5] is 1%. A correction of 0·5 ± 0·5% has been applied to allow for the self-absorption of the sources. The weights of the sources were 0·5–1·0 μg.

RESULTS AND DISCUSSION

The results are summarized in Table 1. The experiment measured directly the ratio of the effective cross-sections of Np^{237} and Au^{197} for the neutron of energy less than about 0·4 eV (sub-cadmium). It is usual to quote cross-sections for 2200-m/sec neutrons, but the ratio of the effective cross-sections cannot be strictly converted to the ratio of 2200-m/sec cross-sections unless the cross-section versus energy curves of both nuclides for subcadmium neutrons are known, and also the neutron energy spectrum of these neutrons. However, if both nuclides have the same cross-section

[4] R. J. ROYSTON, private communication.
[5] B. D. PATE and L. YAFFE, *Canad. J. Chem.* **33**, 929 (1955).

versus energy dependence (e.g., both are "$1/v$"), the 2200-m/sec ratio will be the same as the effective ratio.

TABLE 1.—SUMMARY OF RESULTS

Irradiation number	$Np^{237}(n,\gamma)Np^{238}$	Epi-Cd Activity / Sub-Cd Activity
1	171	0·27
2	175	0·23
3	163	0·25
4	177	0·22
Mean	172	0·24

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The Au^{197} cross-section versus energy dependence is very close to "$1/v$" in the sub-cadmium region.[6] The Np^{237} cross-section also appears to be approximately "$1/v$" in the most important part of the sub-cadmium region, but there is some deviation at energies just below the cadmium cut-off, due to a fairly large resonance at about 0·5 eV. The available data[6, 7] does not seem to be sufficiently precise for a correction to be computed with certainty, and in any case this correction would be small. It has therefore been assumed that the Np^{237} and Au^{197} cross-sections have the same energy dependence for sub-cadmium neutrons, and column (2) of Table 1 gives the "2200 m/sec", values calculated for Np^{237} on this basis, taking the 2200-m/sec value for Au^{197} as 98 barns.[1]

Column 3 gives the ratio of the epi-cadmium to sub-cadmium contributions for Np^{237}. This varies somewhat between irradiations, since the neutron energy distribution is not necessarily always the same, on account of the use of different irradiation positions and of the movement of neighbouring samples, fuel rods, and control rods. The average for the ratio is 0·24, so that resonance-capture in Np^{237} is significant for BEPO neutrons.

The errors due to known causes are estimated to be as follows:

Flux

Weight of gold	±0·5%
β-counting statistics	negligible
Deviations between β sources	±0·5
Film-absorption correction	±0·5
Self-absorption correction	±0·5%
Irradiation time	negligible
Half-life of Au^{198}	negligible
Gold cross-section	±1%

Pu^{238}/Np^{237} ratio

Half-life of Np^{237}	±2%
Half-life of Pu^{238}	±0·5%
Statistics in α-pulse analysis	±1·5%

[6] Selected Reference Material on Atomic Energy, Vol. V. Neutron Cross-Sections. BNL 325 (1955).
[7] Y. B. ADAMCHUK, *et al.* International Conference on the Peaceful Uses of Atomic Energy, Paper 645 (1955).

The random errors compounded by taking the square root of the sum of their squares give a total random error of $\pm 1{\cdot}7\%$ (3 barns). The total systematic error, computed in the same way, is $\pm 2{\cdot}4\%$ (4 barns). The four results shown in column 2 of Table 1 reveal a greater spread than would be expected from the estimated random error. This is probably due to the difficulty in ensuring that the covered and uncovered foils are irradiated in positions of identical flux; not only are there flux gradients in the pile, but these change during irradiations, owing to changes in pile-loading. The random error actually found, i.e., the standard deviation of the set of four results, is $\pm 3{\cdot}5\%$ (6 barns). The overall error, computed from the observed random error and the estimated systematic error, is $\pm 4{\cdot}2\%$ (7 barns). We therefore quote a result of 172 ± 7 barns.

Acknowledgements—The authors wish to thank (Mrs.) K. M. GLOVER and F. J. G. ROGERS for the α-pulse analysis measurements; T. L. MARKIN, A. J. WALTER, and H. H. WILLIS for assistance in preparing and counting the sources; R. J. ROYSTON, of the Theoretical Physics Division, for computing the self-shielding correction in the gold wire. They also thank Dr. S. FRIED, of the Argonne National Laboratory, for being able to refer to his redetermination of the Np^{237} half-life before publication of his results.

J. Inorg. Nucl. Chem., 1956, Vol. 2, pp. 209 to 218. Pergamon Press Ltd., London

RADIATIONS OF PLUTONIUM-246*

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(*Received* 3 *August* 1955)

Abstract—The beta and gamma spectra of Pu^{246} were examined with scintillation spectrometers used in conjunction with multichannel analysers and a coincidence circuit. A decay scheme is presented and the disintegration energy is given as 0·400 ± 0·030 MeV.

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1. INTRODUCTION

THE determination of the disintegration energies and decay schemes of the heavy nuclides is of considerable interest for comparison with the values predicted by the cycles of alpha and beta decay[1] and the energy levels predicted by theory. In this study, the radiations of Pu^{246} were examined by beta and gamma scintillation spectrometry in conjunction with coincidence techniques. Since the Pu^{246} and its 25-min Am^{246} daughter equilibrate rapidly, coincidence measurements were of the utmost importance in revealing radiations of the Pu^{246} which would otherwise have been masked by the higher-energy Am^{246} beta-emitter.[2] Pu^{246} and Am^{246} have been previously reported and identified.[3]

2. EXPERIMENTAL

Sample Preparation

The plutonium was purified by a chemical procedure,[2, 4] utilizing several cycles of reduced and oxidized LaF_3 precipitations and anion-column elutions with a saturated HCl-0·25 M HI solution. Several aliquots of various plutonium samples were removed for half-life measurements. The remainder of the samples was combined, mounted on a rubber hydrochloride film, and used in the following coincidence studies.

Half-life

The gross decay of several aliquots of the purified plutonium samples was followed for at least four months with a methane-flow proportional beta-counter having a 2-in. diameter, 4·8-mg/cm² thick aluminium window. After subtraction of a contribution constituting ~1% of the initial Pu^{246} activity (probably due to the Pu^{241} beta activity or soft gamma radiation from Pu^{239} and Pu^{240}), a value of 10·85 ± 0·02 days (Fig. 1) was obtained for the half-life of Pu^{246} by a least-squares fitting of the data. This is in fair agreement with previously reported values.[3]

Singles Spectra

A study of the beta and gamma radiations of Pu^{246} was very difficult because of the presence of the daughter activity, Am^{246}, and of Am^{241} growing in from the Pu^{241} in the sample. However, from the differences in the gamma spectra of the Pu^{246}-Am^{246} equilibrium mixture (Fig. 2) and the Am^{246} activity alone,[3] gamma-rays of 47, 175, and 215 keV could be attributed to Pu^{246}, although Am^{246} may have a relatively low intensity gamma-ray in the 180-keV region. The presence of a 245-keV

* This work was performed under the auspices of the U.S. Atomic Energy Commission.

[1] R. A. GLASS, S. G. THOMPSON, and G. T. SEABORG, *J. Inorg. Nucl. Chem.* **1**, 1 (1955).
[2] H. L. SMITH, C. I. BROWNE, D. C. HOFFMAN, M. E. BUNKER, and J. P. MIZE, *Radiations of Am^{246}* (to be published).
[3] D. ENGELKEMEIR, P. R. FIELDS, S. FRIED, G. L. PYLE, C. M. STEVENS, L. B. ASPREY, C. I. BROWNE, H. LOUISE SMITH, and R. W. SPENCE, *J. Inorg. Nucl. Chem.* **1**, 345 (1955).

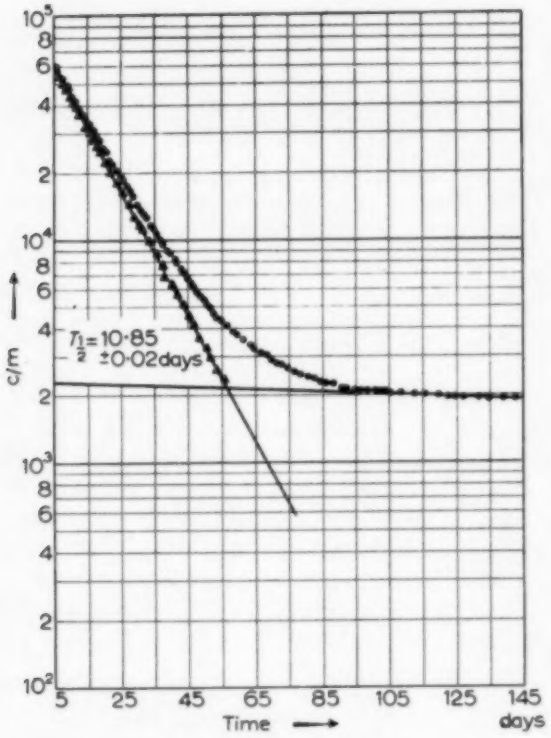

FIG. 1.—Half-life of Pu^{246}.

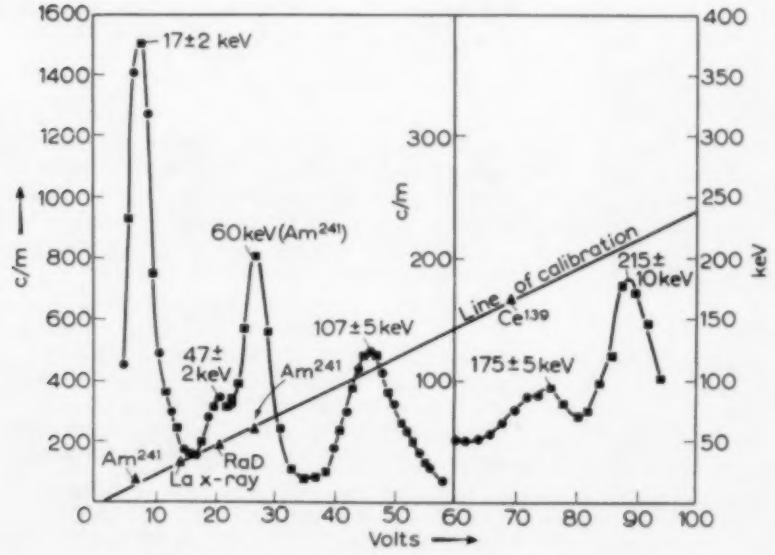

FIG. 2.—Partial gamma singles spectrum of equilibrium mixture.
● and ■ represent overlapping runs.

gamma-ray in the radiations of Am^{246} precludes the definite assignment of radiation of this energy to Pu^{246} decay.

It was impossible to study the Pu^{246} beta spectrum without utilizing coincidence techniques because of the many high-energy Am^{246} beta groups[3] and the Am^{241} and $Pu^{239-240}$ alphas which completely masked the low-energy Pu^{246} beta radiation.

Gamma-gamma Coincidence Studies

A Los Alamos Model-300 coincidence unit[4] and 10- and 100-channel pulse-height analysers were used.[4] The sample was placed in a holder (geometry reproducible to $\pm 5\%$) between two NaI(Tl) crystals (1 in. long by 1½ in. diameter) mounted on DuMont 6292 photomultiplier tubes at 180° to each other inside a thick lead shield. RaD, Am^{241}, and Ce^{139} were used in the energy calibration (Fig. 2).

Since the 47-keV gamma-ray was known to belong only to Pu^{246}, one channel of the coincidence circuit was set from 36 to 48 keV (called the "trigger" region) and the other channel was set at its minimum and maximum values so that the radiation in coincidence with the 47-keV peak could be pulse-analysed (Fig. 3). The gamma spectrum in coincidence with the 180-keV region was similarly obtained (Fig. 4). Table 1 presents a summary of the relative intensities of the gamma-rays in coincidence with each trigger region. Before these gamma intensities can be compared, an absorption correction must be applied for the ~330 mg/cm² aluminium covering on the NaI(Tl) crystals.

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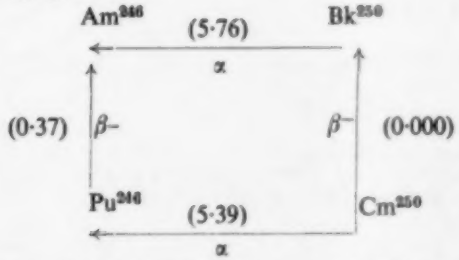
Gamma-beta Coincidence Studies

In the gamma-beta coincidence studies a ½-in. long by 1⅝-in. diameter *trans*-stilbene crystal, packed in Al_2O_3, and covered with 0·2-mil aluminium foil, was used in place of one of the NaI(Tl) crystals. The gain was adjusted to cover a beta-energy range of 50 to about 600 keV, and the beta groups of Co^{60}, Pm^{147}, Zr^{95}, and Nb^{95} were used in the calibration after making Fermi plots of the data.

Using the region of the 175-keV gamma radiation as a trigger, one beta group with an endpoint energy of 150 ± 10 keV was observed (Fig. 5). The rather high-energy component which is also present probably belongs to Am^{246}, since its gamma radiation undoubtedly contributes to the trigger. When the 47-keV gamma peak was used as a trigger, a beta group with an endpoint energy of 330 ± 30 keV was observed, in addition to the 150-keV group (Fig. 6). By integration of the corrected counts per minute obtained from the Fermi plots, the ratio of the 150- to the 330-keV group was found to be 2·7, or 73% of the total beta disintegrations, assuming there is no beta transition to the ground state. Partial half-lives of 14·9 and 40·2 d and log ft values of 6·0 and 7·4 can be calculated for the 150- and 330-keV groups, respectively. These values would seem to indicate first forbidden transitions.

3. DISCUSSION

A decay scheme consistent with the data is shown in Fig. 7. The disintegration energy of $0{\cdot}400 \pm 0{\cdot}030$ MeV agrees within experimental error with the value of 0·37 MeV predicted by the cycle below. None of the energies in this cycle have been determined experimentally; they were estimated by GLASS[1] so as to satisfy the energetics of adjoining cycles.



[4] C. I. BROWNE, D. C. HOFFMAN, W. T. CRANE, J. P. BALAGNA, G. H. HIGGINS, J. W. BARNES, R. W. HOFF, H. L. SMITH, J. P. MIZE, and M. E. BUNKER, *J. Inorg. Nucl. Chem.* 1, 254 (1955).

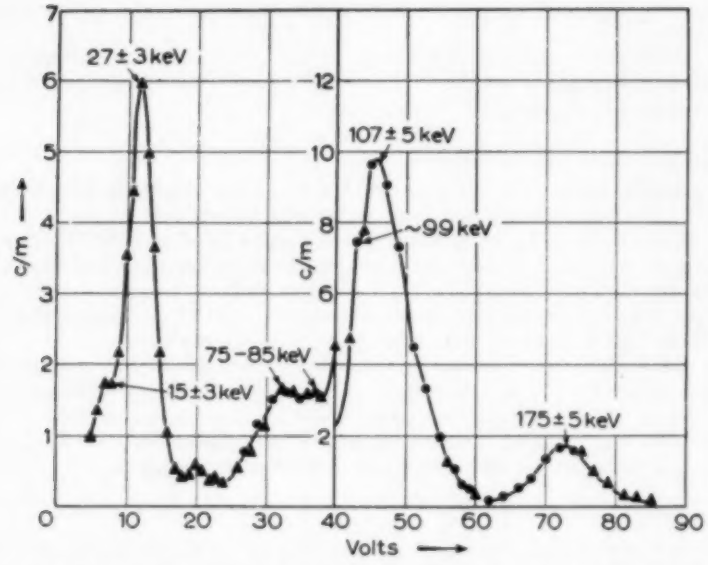


FIG. 3.—Gamma spectrum in coincidence with the 36- to 48-keV gamma region. ▲ and ● represent overlapping runs.

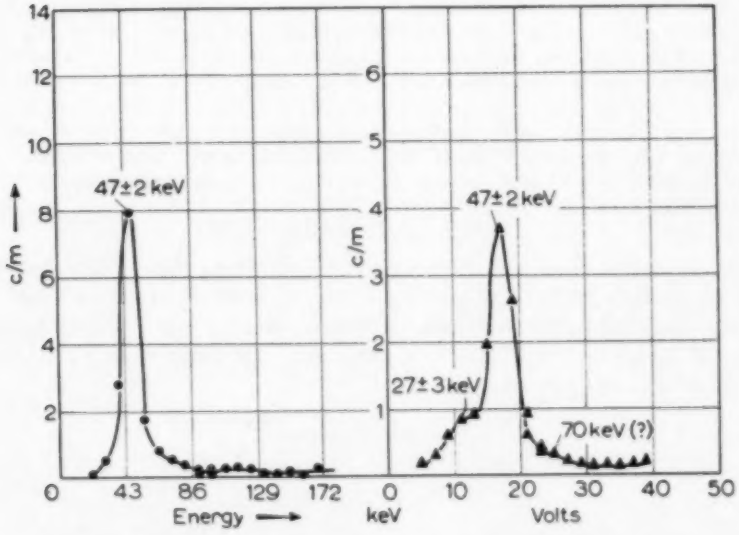


FIG. 4.—Gamma spectra in coincidence with the 155- to 185-keV gamma region. Gamma spectrum in coincidence with 155–185-keV region—●. Similar spectrum taken at higher gain—▲.

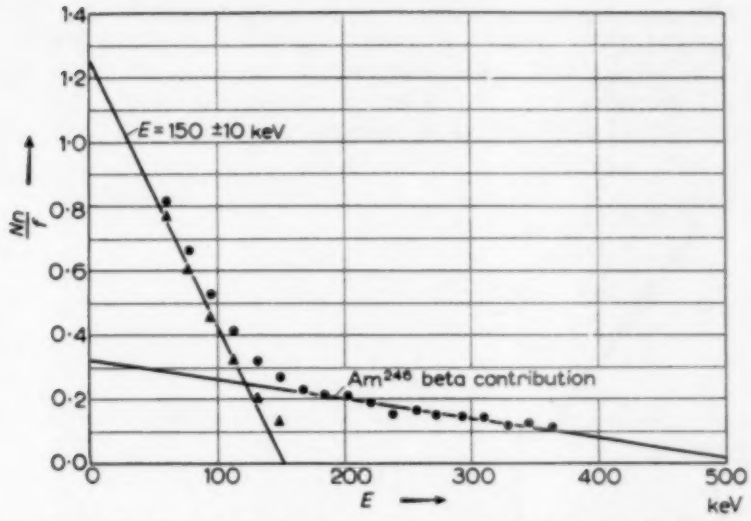


FIG. 5.—Fermi plot of beta spectrum in coincidence with the 170- to 190-keV gamma region.

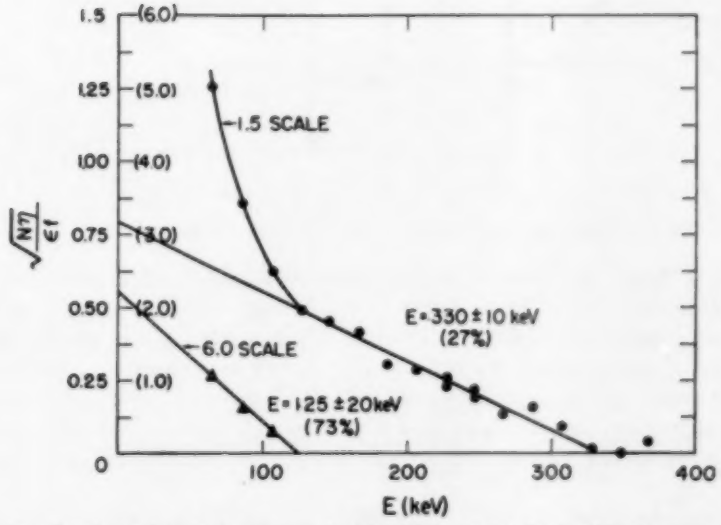


FIG. 6.—Fermi plot of beta spectrum in coincidence with the 36- to 48-keV gamma region.
Unresolved points—●.
After subtraction of 330-keV component—▲.

Since the limits of error on the 330-keV beta are ±30 keV, it is impossible to determine conclusively by energy considerations whether it feeds a 47- or a 74-keV level. One cannot trigger with the 27-keV gamma region in order to determine if the 330-beta is in coincidence with it without appreciable contributions to the trigger from the 47-keV gamma or *L* X-rays. Neither is it possible to specify whether the lowest energy level is 27 or 47 keV, but it has been postulated to be 27 keV, which then gives levels at 27 and 74 keV.

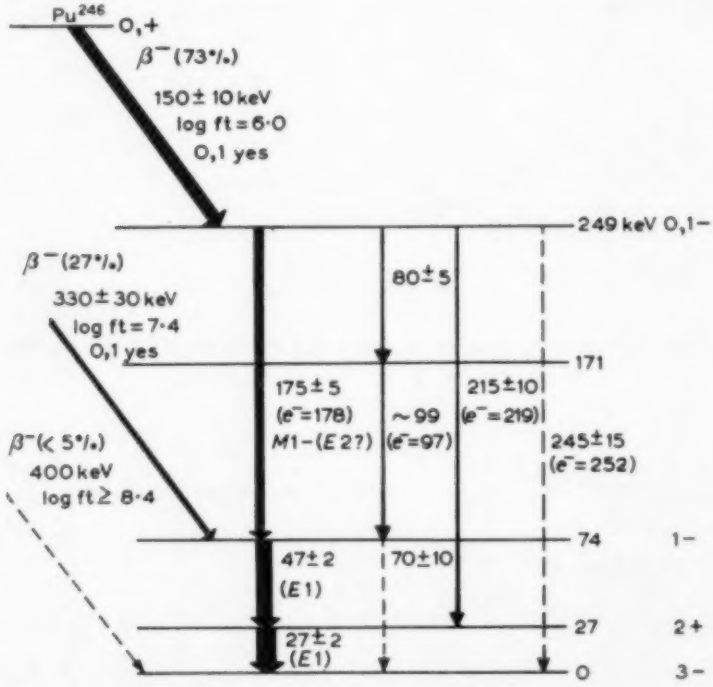


FIG. 7. Partial decay scheme of Pu^{246}. $E_{dis} = 0{\cdot}400 \pm 0{\cdot}030$ MeV.

The 27- and 175-keV gammas were found to be in coincidence with the 47 (Table 1) and constitute one method of de-excitation of the 249-keV level. A 107-keV peak, which is probably mostly *K* X-radiation from the 175-keV gamma, and a complexity on the low side of this at about 99 keV, as well as one or two gammas in the 75- to 85-keV region (there may be some contribution to this region by lead X-rays since the sample and detectors are enclosed in a lead housing), also are observed in coincidence with the 47-keV gamma. These may provide an alternate cascade out of the 249-keV level.

In coincidence with the 155- to 185-keV region are the 27- and 47-keV gammas and possibly a 70-keV gamma of very low intensity (Fig. 4) which may also de-excite the 74-keV level.

A previous magnetic-lens beta-spectrometer study of a Pu^{240}-Am^{246} equilibrium sample[2] showed *K* and *L* conversion lines at 51 and 156 keV respectively, corresponding to a 178 ± 2-keV gamma in plutonium with a *K*/*L* ratio of 4·8. This indicates an *M*1 or *E*1 transition if one assumes no appreciable contribution to either

TABLE 1

Trigger region	Observed gammas keV	Integrated intensity	Absorber correction
36–48 keV	15 ± 3 (*L* X-rays)	2·4	
	27 ± 3	16·4	2·0
	75–85	8·6	1·05
	99 ± 5	—	1·05
	107 ± 5	47·4	1·05
	175 ± 5	8·0	1·05
155–185 keV	27 ± 3	2·5	2·0
(Higher gain in nontrigger channel)	47 ± 2	9·8	1·20
	70 (?)	⩽0·015	1·05

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line from Am^{246} in this region. (Extrapolation of ROSE's K/L ratios[5, 6] gives 6·3 for an $M1$, 2·5 for an $M2$, 4·8 for an $E1$, and 0·2 for an $E2$ transition at $Z = 95$ and 178 keV.) Lines at 65, 74, 94, 114, and 126 keV were also found but none of them corresponded to the K and L lines of a given gamma. Of course, it is impossible to state for certain which lines belong to Pu^{246} and which to Am^{246}. However, the conversion line at 74 keV could be the L line of a 95-keV plutonium gamma which would support the doubtful 99-keV gamma seen in coincidence with the 47-keV region. The 94 and 127-keV lines might be the K lines of 219- and 252-keV gammas which would support the existence of transitions from the 249-keV level to the 27-keV level and to the ground state.

By assuming that all the 107-keV radiation observed in coincidence with the 45-keV gamma is K X-radiation from the 178-keV gamma, the relative intensities given in Table 1 permit a calculation of its K conversion coefficient as about 6. By extrapolation of ROSE's tables of K conversion coefficients for $Z = 95$, values of 8·1 for an $M1$, ~2 for an $E5$, on down to 0·2 for an $E2$ and 0·1 for an $E1$ are obtained. These values seem to support the $M1$ assignment over an $E1$, even though the agreement is not good. (The extrapolation may be poor, and accurate integration of the areas involved is difficult.) If one assumes that the 74-keV level is de-excited principally through the 27–47-keV cascade, a value of $\leqslant 1{\cdot}9$ is obtained for the 27-keV conversion coefficient and $\leqslant 0{\cdot}23$ for the 47, since the ratio of the 27- to the 47-keV gamma is about 0·4 (Table 1) after absorption corrections are made (Appendix A).

Extrapolation to $Z = 95$ of the tables of L conversion coefficients of ROSE[5, 6] and of GELLMAN, GRIFFITH, and STANLEY[7] gives 0·85 for an $E1$, 200 for an $E2$, and 45 for an $M1$ at 47 keV, and 3·3 for an $E1$, 2100 for an $E2$, and 250 for an $M1$ at 27 keV. This indicates that the 27- and 47-keV transitions are probably $E1$. If this is true, their conversion coefficients are too low, which could be due to assuming that the 249 level decays principally through the 175-keV gamma. Assuming 3·3 and 0·85 for these conversion coefficients would require K/L for the 175 to be 1·1 if all the

[5] M. E. ROSE, G. H. GOERTZEL, B. I. SPINRAD, J. HARR, and P. STRONG, *Phys. Rev.* **83**, 79 (1951).
[6] M. E. ROSE, privately circulated tables.
[7] H. GELLMAN, B. A. GRIFFITH, and J. P. STANLEY, *Phys. Rev.* **85**, 944L (1952).

249-level decays through the 175-keV gamma (see Appendix A). This is between the values for $M2$ and $M3$ at $Z = 95$. From the K conversion coefficient and K/L ratio, $M2$ and $M3$ transitions appear to be definitely eliminated. However, if the beta intensities are wrong or if much of the 249-keV level is de-excited other than through the 178-keV gamma, the calculated K/L conversion ratio would change considerably. Assuming $K/L = 4{\cdot}8$, it was calculated (Appendix A) 0·49/0·73, or 67·1% of the 249-keV level decays through the 175-keV gamma, while the remainder must be divided principally among the 252-, the 219- and 27-, and the 96- and 80-keV modes.

In order to try to set an upper limit on a 400-keV beta ground-state transition, the area of the Pu^{246} betas was calculated from the areas of the K and L conversion lines of the 175-keV transition and compared with the area of the Am^{246} beta spectrum as obtained from the magnetic spectrometer data[2] (see Appendix B). Since the Pu^{246}-Am^{246} were in equilibrium, the disintegrations per minute of the Am^{246} betas should equal the disintegrations per minute of the Pu^{246}, and the two areas should be equal within the accuracy of the method if there is no beta ground-state transition. The calculated Pu^{246} area would be too small if the ground-state transition is appreciable. However, it was 58·0 relative to 50·8 for the Am^{246}, or about 14% too high, which probably merely reflects the inaccuracies involved in the calculation and the various conversion coefficients. However, from a consideration of these errors, the ground-state beta transition probably constitutes less than 5% of the total decay, corresponding to a partial half-life of $\geqslant 200$ d, and a $\log ft \geqslant 8{\cdot}4$. This would indicate a second forbidden or higher transition. Although they could not be uniquely specified, spin assignments consistent with the transition types were assigned to the various levels (Fig. 7) where possible.

Acknowledgements—The authors are indebted to Dr. R. W. SPENCE for his continued interest and encouragement, and to FRANCINE LAWRENCE and LOUISE HARRIS for their assistance in the chemical purification of the sample.

APPENDIX A

The 27- and 47-keV gamma conversion coefficients were calculated as follows:

$$(e^- + \gamma)_{27} = (e_K^- + e_L^- + \gamma)_{175}\left(\frac{1{\cdot}00}{0{\cdot}73}\right) \qquad \left(\text{The ratio of betas feeding these levels is } \frac{1{\cdot}00}{0{\cdot}73}\right).$$

$$e_{27}^- = \frac{(e_K^- + e_L^- + \gamma)_{175}}{0{\cdot}73} - \gamma_{27}$$

Using $(K/L)_{175} = 4{\cdot}8$ as determined experimentally, and from Table 1, $\gamma_{175} = 8{\cdot}0$; $e_{K_{175}} < \gamma_{197} < 47{\cdot}4$; $e_{L_{175}} < \frac{47{\cdot}4}{4{\cdot}8} < 9{\cdot}9$; $\gamma_{27} = 16{\cdot}4$ gives:

$$e_{27}^- < \frac{57{\cdot}3 + 8{\cdot}0}{0{\cdot}73} - 16{\cdot}4\left(\frac{2{\cdot}0}{1{\cdot}05}\right) \quad \text{(The last term is the absorption correction.)}$$

$$e_{27}^- < 58{\cdot}3$$

$$\frac{e_{27}^-}{\gamma_{27}} < 1{\cdot}87$$

From Table 1, 155- to 185-keV trigger:

$$\frac{\gamma_{27}}{\gamma_{47}} = \frac{2{\cdot}5}{9{\cdot}8}\left(\frac{2{\cdot}0}{1{\cdot}2}\right) = 0{\cdot}43$$

then, assuming $(e^- + \gamma)_{27} = (e^- + \gamma)_{47}$ gives:

$$e_{47}^- = e_{27}^- + \gamma_{27} - \gamma_{47}$$

$$e_{47}^- \leqq 1{\cdot}87\gamma_{27} + \gamma_{27} - \frac{\gamma_{27}}{0{\cdot}43} \leqq 0{\cdot}54\gamma_{27}$$

$$\frac{e_{47}^-}{\gamma_{47}} \leqq \frac{0{\cdot}54\gamma_{27}}{\gamma_{47}} \leqq 0{\cdot}54(0{\cdot}43) \leqq 0{\cdot}23$$

Assume

$$\frac{e_{27}^-}{\gamma_{27}} = 3{\cdot}3;\ e_{27}^- = 3{\cdot}3(31{\cdot}2) = 103{\cdot}0$$

But:

$$e_{27}^- = \frac{e_{K_{175}}^- + e_{L_{175}}^- + \gamma_{175}}{0{\cdot}73} - \gamma_{27}$$

$$103 = \frac{47{\cdot}4 + e_{L_{175}}^- + 8}{0{\cdot}73} - 31{\cdot}2$$

$$e_{L_{175}}^- = (134{\cdot}2)0{\cdot}73 - 55{\cdot}4 = 42{\cdot}6$$

$$\text{then } \left(\frac{K}{L}\right)_{175} = \frac{47{\cdot}4}{42{\cdot}6} = 1{\cdot}1 \text{ but } \frac{K}{L} \text{ should} = 4{\cdot}8.$$

If one takes $(K/L)_{175} = 4{\cdot}8$ as determined experimentally, and assumes the conversion coefficient for the 27-keV gamma is 3·3, as it should be for an $E1$ transition, it is calculated as shown below that instead of 0·73 of the decay going through the 175-keV gamma, this value must be 0·49 relative to 1 for the 27-keV gamma. Thus, 0·49/0·73 or 67% of the 249-keV level decays through the 175-keV gamma, and the remainder through the 249-, 222- and 27-, or 96- and 80-keV gammas.

$$(e^- + \gamma)_{27} = (e_K^- + e_L^- + \gamma)_{175}\left(\frac{1{\cdot}00}{x}\right)\left(\begin{array}{l}\frac{1{\cdot}00}{x} \text{ is the ratio of decay}\\ \text{through the 27- relative to}\\ \text{the 175-keV } \gamma.\end{array}\right)$$

$$e_{L_{175}}^- = \frac{47{\cdot}4}{4{\cdot}8} = 9{\cdot}88$$

$$\frac{1}{x} = \frac{(e^- + \gamma)_{27}}{(e_K^- + e_L^- + \gamma)_{175}} = \frac{134{\cdot}2}{65{\cdot}3}$$

$$x = 0{\cdot}49$$

Using this value in the calculation for e_{27}^- and e_{47}^-, assuming they are fed nearly equally gives:

$$e_{27}^- = 3{\cdot}3\gamma_{27}$$

$$e_{47}^- = e_{27}^- + \gamma_{27} - \gamma_{47} = 3{\cdot}3\gamma_{27} + \gamma_{27} - \frac{\gamma_{27}}{0{\cdot}43}$$

$$e_{47}^- = 4{\cdot}3\gamma_{27} - 2{\cdot}3\gamma_{27} = 2{\cdot}0\gamma_{27}$$

$$\frac{e_{47}^-}{\gamma_{47}} = \frac{2{\cdot}0\gamma_{27}}{2{\cdot}3\gamma_{27}} = 0{\cdot}87 \qquad \left(\frac{e_L^-}{\gamma}\right)_{47} \text{ was found to be 0·85 for an } E1 \text{ by extrapolation of Rose's data.}$$

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APPENDIX B

From magnetic spectrometer data:

$$\text{Area } Am^{246} \text{ betas} = 50{\cdot}8$$

$$\text{Area } (e_K^- + e_L^-)_{175} = 25$$

$$K/L = 4{\cdot}8$$

$$e_K^- + e_L^- = 1{\cdot}21 e_K^-$$

$$\frac{e_K^-}{\gamma} = 6 \text{ (from Table 1)}$$

Therefore:

$$\frac{e_K^- + e_L^-}{\gamma} = 6(1{\cdot}21) = 7{\cdot}3$$

$$\frac{\Sigma e^-}{\Sigma e^- + \gamma} = \frac{7{\cdot}3}{8{\cdot}3} = 0{\cdot}88$$

but area $\Sigma e^- = 25$

Therefore, total 175-keV transition

$$= \Sigma e^- \Big/ \frac{e^-}{\Sigma e^- + \gamma} = \Sigma e^- + \gamma = 28{\cdot}4$$

However, only 0·49 of total observed Pu^{246} beta decay goes through 175-keV gamma. Therefore, total Pu^{246} area = 28·4/0·49 = 58·0, compared to 50·8 for Am^{246}.

J. Inorg. Nucl. Chem., 1956, Vol. 2, pp. 219 to 222. Pergamon Press Ltd., London

ACTIVITY RATIOS OF THE Br^{80} ISOMERS, STUDIED BY MEANS OF AN ALUMINA ADSORPTION PROCESS

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(*Received* 11 *November* 1955; *in final form*, 16 *December* 1955)

Abstract—Experiments on neutron-irradiated *n*-propyl bromide, which was purified by adsorption on alumina, indicate different chemical behaviour of the two Br^{80} isomers. This difference is shown in the activity ratios of the two isomers in the unwashed material and in the washed product obtained by passing the bromide through an alumina column.

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Whether the two isomers of Br^{80}, resulting from radiative neutron capture, show different chemical behaviour as a function of the energy of the incident neutrons, is a subject which is still disputed.[1–11] This paper further elucidates the problem.

EXPERIMENTAL

Purification of Materials

A NEW method of purification of the materials was used. If purification precedes irradiation by an appreciable time-interval, one cannot be certain that no change occurs between the moment of purification and the moment of using. Indeed it is well known how unstable organic bromides are.

In the experiments summarized below, *n*-propyl bromide (L. Light and Co., Ltd., London) was purified by adsorption on alumina, immediately before each irradiation. It is believed that alumina adsorbs most of the impurities which might be present in the sample.

The alumina was MERCK's, specially prepared for chromatographic adsorption analysis according to BROCKMANN's method. The powder is composed of very small-sized particles (200-mesh), to increase the adsorptive power. It has a slightly alkaline reaction, and it can exchange ions through the H^+ (H_3AlO_3) and Na^+ (Na_3AlO_3) it contains. As alumina has an amphoteric character, it adsorbs negative as well as positive ions, and eliminates the free ionized bromine which may already be present in the bromide. A "nonspecific" adsorption (analogous to that of activated charcoal) eliminates the un-ionized free bromine. It has also been proved that alumina preferentially adsorbs olefinic rather than saturated compounds.[12]

It may thus be assumed that passage of the *n*-propyl bromide through alumina removes all the impurities which can harm the experiments or falsify the results, i.e., water-soluble bromine compounds and the olefins which could provoke secondary reactions with radioactive bromine radicals.

Immediately before each irradiation, the *n*-propyl bromide was passed through a column of fresh alumina 2 cm in diameter and 20 cm high.

Treatment of the Irradiated Products

It seems that an adsorption process can advantageously replace the washing of the irradiated products such as was used by WILLARD and by CAPRON, the latter washing with pure water, the

[1] J. C. W. CHIEN and J. E. WILLARD, *J. Amer. Chem. Soc.* **76**, 4735 (1954).
[2] M. S. FOX and W. F. LIBBY, *J. Chem. Phys.* **20**, 487 (1952).
[3] F. S. ROWLAND and W. F. LIBBY, *J. Chem. Phys.* **21**, 1495 (1953).
[4] P. C. CAPRON, *Bull. Acad. Roy. Belg.* **27**, 524 (1941).
[5] P. C. CAPRON, E. CRÈVECOEUR, and M. FAES, *J. Chem. Phys.* **17**, 349 (1949).
[6] P. C. CAPRON and E. CRÈVECOEUR, *Bull. III^e Congr. Nat. Sc. Brux.* 214 (1950).
[7] P. C. CAPRON and A. J. VERHOEVE-STOKKINK, *Phys. Rev.* **81**, 336 (1951).
[8] P. C. CAPRON and E. CRÈVECOEUR, *J. chim. phys.* **49**, 29 (1952).
[9] P. C. CAPRON and Y. OSHIMA, *J. Chem. Phys.* **20**, 1403 (1952).
[10] P. C. CAPRON and E. CRÈVECOEUR, *J. Chem. Phys.* **21**, 1843 (1953).
[11] P. C. CAPRON and L. J. GILLY, *J. chim. phys.* **52**, 505 (1955).
[12] H. H. STRAIN, *Chromatographic Adsorption Analysis*, Interscience Publishers Inc., New York, N.Y., 1945, p. 15.

former with solutions of Br_2, HBr, or Na_2SO_3. An adsorption process avoids the possibility of parasitic reactions between the additives and the active radicals which are formed during irradiation. Some of these ionized particles have rather long lifetimes.[13] This was confirmed by some unpublished experiments, using an electric field, which indicated a half-life for these ions of between 6 and 8 h. These experiments were done on Br^{80} (4·4 h) and Br^{82} (36 h).

Passage through an alumina column is analogous to washing, because the more or less ionized particles and fragments which enter into the aqueous phase during washing can also be held by the alumina column, as the following experiments show. *n*-Propyl bromide was exposed for 3 h to slow neutrons produced by the 2·4-curie Ra-Be source, surrounded with paraffin. Two gold plates (4·5 cm × 4·5 cm) at a potential difference of 400 V were placed in the irradiated liquid at a distance of 1 cm from each other. Gold was chosen because of its weak chemical affinity to bromine, thus avoiding secondary reactions. The electric field was applied for 10 min. The activity deposited on the plates was rather high in all three bromine activities. On the other hand, if the irradiated product was first filtered through an alumina column before the electric field was applied, neither the cathode nor the anode showed any activity other than that due to Br^{80} (18 min) formed by isomeric transition after the filtration and during the electromigration.[14] This proved that the alumina adsorbed all the ionized bromine fragments produced during the irradiation. It also showed that, since free Br^{80} (4·4 h) is totally absent, the combined Br^{80} (4·4 h) is not affected by the electric field and that no adsorption on the gold plates occurs. Consequently, alumina adsorption may be used instead of washing of the irradiated products.

The dimensions of the alumina column were: height = 10 cm, diameter = 1 cm, volume = 7·8 ml. As the 7·4-g alumina, which fills the column, occupies about 2 ml, the free space is 5·8 ml. The percolation rate was 2 ml/min. The first 20 ml (three to four times the free volume) were discarded, to ensure that the sample used had passed right through the column.

In order not to exceed the adsorption capacity, a new column was used for each experiment.

Irradiation Time

LIBBY[2, 3] has suggested that the difference in the chemical composition of the isomers observed by CAPRON could arise from the fact that with irradiations of 3 h, and even of 1 h, the average lives of the radioactive nuclei are very different, so the probability of reactions involving combined Br^{80} (4·4 h) is greater.

In these experiments an irradiation time of 20 min was chosen: the resulting nuclei have then an average life $\theta = [1 - e^{-\lambda t}(\lambda t + 1)]/(1 - e^{-\lambda t})$ (t = irradiation time), which is equal to 8·8 min for Br^{80} (18 min) and 10·3 min for Br^{80} (4·4 h). These are not very different.

It is better to work with ratios of activities $R = Br^{80}$ (18 min)/Br^{80} (4·4 h), than with retentions. The ratios can be determined from a single experiment, while the retentions require two, with increased possibility of error.

An irradiation time shorter than 20 min should be avoided, because the activity of Br^{80} (4·4 h) would be very weak and the measurements too imprecise.

The samples (70 ml of *n*-propyl bromide) were irradiated under the same conditions as in the recent experiments by CAPRON and GILLY.[11] Slow neutrons were produced by a radium-beryllium source of 2·4 curie, surrounded by a paraffin block of 37-cm height and 48-cm diameter, inside of which the sample was contained in a 250-ml Erlenmeyer flask; it was separated from the source by 8 mm of plexiglass and 2 cm of paraffin. The irradiation with fast neutrons was carried out at 0·5 cm from the same source, but after all the paraffin had been removed.

The activity was measured by Geiger-Müller liquid counters (20th Century Electronics Ltd., thin glass wall), each of which was connected by a preamplifier to direct recorders, constructed in the Louvain Laboratories. A camera automatically recorded the activity every 3rd minute until the 75th minute, and every 15th minute until the 420th minute (times measured from the end of the irradiation). No correction for the resolving time (10^{-6} min) seemed necessary.

After the background activity had been deducted, the calculations were made by the integral method.[10] For a 20-min irradiation, the Br^{82} (36 h) activity can be neglected, as has been verified. The activity at zero time of Br^{80} (4·4 h) was calculated from the number of counts recorded between

[13] FAY and PANETH, *J. Chem. Soc.* 384 (1936).
[14] G. KAYAS, *Thèses* (Masson et Co, Editeurs, Paris, 1952), p. 36.

the 180th and 420th min; the activity between the 75th and 120th min, the Br^{80} (4·4 h) disintegrations being subtracted, then gave the initial Br^{80} (18 min) activity. Correction for the isomeric transition is avoided, as previous experiments have shown that after 75 min, equilibrium between Br^{80} (4·4 h) and its isomeric transition Br^{80} (18 min) has been attained.

RESULTS

The results of the experiments are summarized below: (C_0 = activity at $t = 0$; R = ratio of the activities).

TABLE 1.—SLOW NEUTRONS

Unfiltered on alumina			Filtered on alumina		
C_0 (18 min)	C_0 (4·4 h)	R	C_0 (18 min)	C_0 (4·4 h)	R
15,764·8	560·6	28·1	8,274·8	355·8	23·3
16,607·5	729·8	22·8	8,738·2	321·8	27·2
12,106·7	507·9	23·8	9,978·8	353·9	28·2
15,547·4	578·5	26·9	9,868·8	416·2	23·7
17,319·3	622·0	27·8	11,548·5	435·3	26·5
17,195·9	653·4	26·3	11,994·2	424·0	28·3
18,797·5	709·0	26·5	11,369·7	441·5	25·8
$R_M = 26·0 \pm 0·7$			$R_M = 26·1 \pm 0·7$		

TABLE 2.—FAST NEUTRONS

Unfiltered on alumina			Filtered on alumina		
C_0 (18 min)	C_0 (4·4 h)	R	C_0 (18 min)	C_0 (4·4 h)	R
2,921·2	96·5	30·2	1,462·2	82·2	17·8
2,410·8	104·0	23·2	1,704·8	93·6	18·2
3,228·3	131·3	24·6	918·3	37·7	24·3
2,813·7	122·8	23·0	1,991·0	79·2	25·0
2,720·5	106·7	25·5	1,876·9	88·1	21·3
2,740·6	116·7	23·5	1,707·3	92·3	18·5
3,275·3	127·3	25·7	1,509·2	89·2	16·9
2,472·0	126·1	19·6	1,689·7	81·4	20·7
4,617·5	168·1	27·4	1,754·3	97·2	18·0
5,817·0	199·0	29·2	1,525·2	85·9	17·8
$R_M = 25·2 \pm 0·9$			$R_M = 19·8 \pm 0·8$		

The errors for the mean ratio values are the root-mean-square deviations.

DISCUSSION

The results agree in all points with those obtained by CAPRON in earlier work, in which washing with water was used in place of alumina adsorption.

After a 20-min irradiation with slow neutrons, the activity ratios seem to be equal in the washed and the unwashed products, while they differ for fast-neutron bombardment. The Br^{80} isomers thus behave differently, and their behaviour is a function of the energy of the incident neutrons.

Furthermore, if any significance can be attached to the slight difference in the average lives of the two isomers, then the fact that no difference in the activity ratios is found on irradiation with slow neutrons also implies a difference in the chemical behaviour of the two isomers.

It should be noted that the ratios determined in these experiments with *n*-propyl bromide vary in the opposite direction to those reported by CAPRON and GILLY,[11] who used *iso*-propyl bromide. However, unpublished experiments by the same authors using mono-bromobenzene show differences in the same direction as those found above with *n*-propyl bromide. This may imply that straight-chain bromides react differently from branched ones.

In conclusion, it seems that these experiments confirm CAPRON's previous opinion that the two isomers of Br^{80} react differently according to the energy of the incident neutrons, and that, consequently, the recoil atom has a different energy or is in a different state of ionization for the two isomers. This is quite plausible if one remembers that the existence of different capture-levels for the two isomers has been proved for fast-neutron bombardments.[7]

Acknowledgement—The authors wish to express their sincere gratitude to the Union Minière du Haut Katanga, which has generously lent the radium-beryllium source used in these experiments.

They also wish to thank G. MICHOTTE for the construction of the electronic apparatus.

J. Inorg. Nucl. Chem., 1956, Vol. 2, pp. 223 to 228. Pergamon Press Ltd., London

THE ANALYSIS OF COMPLEX MIXTURES OF ELEMENTS RESULTING FROM THE IRRADIATION OF FISSILE MATERIALS

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(*Received* 1 *December* 1955)

Abstract—An analytical scheme for the separation of complex mixtures of mainly fission-product elements on the semimicro scale is described. The method has been used by many operators, who have obtained satisfactory chemical yields of separated radiochemically pure carrier-borne and sometimes carrier-free nuclides. The method has proved successful even in the presence of gross quantities of foreign matter.

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INTRODUCTION

MANY authors have described procedures by which radioactive nuclides can be separated from target elements with the aid of added carriers, and purified radiochemically prior to estimation by radioactive counting.[1, 2, 3] However, there are few published methods by which many radio-elements may be separated from the sample, a procedure which is essential whenever the maximum information must be obtained from a limited total activity, the components of which may be of relatively short half-life. An alternative case arises in the estimation of radio-nuclides in large masses of inactive materials, when the necessity of ensuring isotopic exchange with small quantities of added carriers limits the total quantity of material, and thus of activities in one analysis. Theoretically, such procedures may be derived from the classical methods described by SCHOELLER and POWELL[4] or NOYES and BRAY,[5] for each case as it arises, but in practice it is a great convenience to have a well-tried basic system making use of, for example, recent ion-exchange techniques, and restricted to those elements usually of greatest interest in the chemistry of nuclear fission.

EXPERIMENTAL

It is assumed that the approximate shape of the fission-product yield-mass curve and evidence of the formation of some other significant elements is required for the case of a bombardment of small quantities of a heavy element. For this purpose a separation of the elements, Rb, Sr, Y, Zr, Mo, Ru, Ag, Cd, Cs, Ce, Ba, La, Pr, Nd, Pm, Sm, Eu, U, Np, Pu might be expected to yield a great part of the required information from a single sample. When used for samples containing soil, rock, organic material, etc., the procedures must allow separation of the required elements from the constituents of the matrix and, at the same time, ensure that isotopic exchange of carrier and carrier-free material is complete. For this reason, a fusion had been used initially, and it has been shown

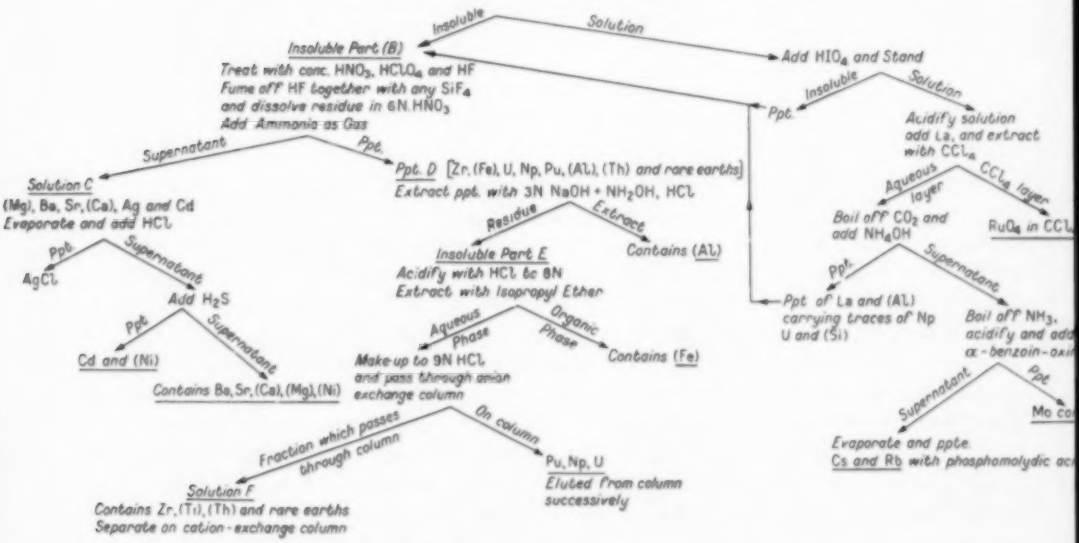
[1] W. WAYNE MEINKE, United States Atomic Energy Commission Reports A.E.C.D. 2738 (1949), A.E.C.D. 2750, (1949), and A.E.C.D. 3084, (1951).
[2] C. D. CORYELL and N. SUGARMAN, *N.N.E.S.* Vol. IV-9 Radiochemical studies: *The Fission Products* (McGraw-Hill, New York) (1951).
[3] J. KLEINBERG, *Collected Radiochemical Procedures*: Los Alamos Scientific Laboratory Report LA-1566 (1953).
[4] W. R. SCHOELLER and A. R. POWELL, *The Analysis of Mineral Ores and of the Rarer Elements*, Griffin, London, (1940).
[5] A. A. NOYES and W. BRAY, *A System of Qualitative Analysis for the Rare Elements*, Macmillan, London (1948).

that the quantities of reagent detailed below will successfully deal with 250-mg samples of rock even if they contain fused rutile or alumina. Of course, the constitution of the matrix must be taken into account when estimating chemical yields of carriers, and small modifications to volumes may be necessary in the scheme depending on the matrix composition. An outline of the separation procedure is given in Fig. 1: the detailed method follows.

1. FUSION AND LIXIVIATION

All the reagents used were of A.R. quality. A 4 × 4-cm nickel crucible and lid were fired in a muffle-furnace at approx. 1000°C for 30 min in order to oxidize the surface of the crucible to a resistant oxide layer. To the cooled crucible were added known quantities of the carrier elements (approx.

FIG. 1.—Outline of separation scheme.



Note: Elements given in parentheses are those which derive from common rocks, and enter the analysis with the inorganic matrix.

10 mg or, in the case of transuranic elements, known amounts of tracer isotopes), usually in solution as nitrates, together with the solid sample or a solution of the target element usually of not more than 20-mg weight. The liquid was then evaporated by heating under an infra-red lamp, and the drying process was completed by heating for a short time in the muffle-furnace at 500 ± 10°C. The whole mass was then fused for 2 h at 500 ± 10°C with a mixture of 1 g KOH, 1 g K_2CO_3, and 2 g KNO_3, the liquid melt so formed being mixed by occasional swirling round the crucible, which was covered throughout, since on occasion slight spitting occurred at the beginning of the fusion.[6] The crucible was cooled and the melt leached with a minimum of hot water, using a transfer pipette to stir the suspension and then to transfer it to a 40-ml centrifuge tube. The crucible and lid were washed with hot water and the washings were added to the centrifuge tube to give a total volume of approx. 15 ml. The insoluble part was then centrifuged hard and the supernatant solution transferred to another 40-ml centrifuge tube together with two aqueous washes of the insoluble residue *B*. The crucible and lid were finally washed twice with 3-ml portions of concentrated nitric acid, the washings being added to the insoluble part *B* from the aqueous lixiviation; this concentrated-acid washing

[6] J. HERRINGTON and R. POWELL. Unpublished work on the exchange of radiogenic ruthenium with carrier ruthenium in caustic alkaline fusion mixtures.

ensured complete removal of any tracer quantity of heavy elements and any metallic Ag formed in the melt. Crucible and lid then showed negligible radioactive content when monitored.

2. TREATMENT OF LIXIVIATE

(*Containing* Mo, Ru, Alkali metals, some Np, U, Zr (Al)).

Periodic acid (0·1 g dissolved in a little water) was added to the lixiviation liquor to oxidize ruthenium to its highest valency state, and the solution was allowed to stand for 20 min at least. A slight precipitate of zirconium iodate was removed by centrifuging, washing with a little water, and transferring to the insoluble fraction *B*, using concentrated nitric acid. The presence of zirconium at this point may be due to the tendency of the hydroxide to form colloids, or to its amphoteric nature. The supernatant solution and washings were cautiously acidified with 6 N HNO_3 until the orange colour of $KRuO_4$ changed to the pale yellow of RuO_4, approx. 5 mg. Lanthanum carrier was added in 1 ml of solution, and the RuO_4 extracted by successive 10-ml portions of carbon tetrachloride, precipitates in the aqueous phase being ignored. The organic extracts were combined, washed with 3 ml water, and treated with 1 drop of methyl alcohol to precipitate black *ruthenium oxide* from solution; this was washed and dissolved by heating with caustic potash solution containing KIO_4. On cooling and acidifying with nitric acid, RuO_4 was again extracted into carbon tetrachloride. Ruthenium was recovered from the organic layer by exhaustive washing with small portions of concentrated hydrochloric acid until the acid layer became no more than pink; the aqueous-acid layers were then combined, evaporated just to dryness, the residue dissolved in 3 ml of water, and RuI_3 precipitated from the hot solution by addition of 3 ml 10% potassium iodide in water. After standing in a hot-water bath for 1 h the precipitate was washed with water, alcohol, and ether, and mounted for counting.

The acid-aqueous phase, after removal of ruthenium in carbon tetrachloride, was boiled to remove all CO_2. To the cooled solution, CO_2-free concentrated ammonium hydroxide solution, or ammonia gas, was added to precipitate $La(OH)_3$ and $Al(OH)_3$, which also carried any neptunium or uranium present in trace quantities. The precipitate was centrifuged, washed with a little water, and added to the insoluble fraction *B*, using concentrated nitric acid. The supernatant solution and washings were boiled to remove ammonia, and the cooled solution was acidified with 6 N HNO_3; molybdenum was then precipitated by addition of 3 ml of 2% alcoholic α-benzoin-oxime, and the precipitate was centrifuged off and washed with 5 ml 1 N HNO_3. The *molybdenum precipitate* was further purified before β-counting,[1] and was mounted as the oxinate. The supernatant solution and washings were evaporated to dryness and treated for recovery of *caesium and rubidium* by the method of SCOTT and FURMAN,[7] using phosphomolybdic acid. The two elements having been removed from the much larger quantities of potassium, may be separated by the ion-exchange method of KAYAS[8] or STEEL.[9]

3. TREATMENT OF INSOLUBLE RESIDUE *B*

(*Containing* Ba, Sr, Ag, Cd, Y, *Rare Earths*, Pu, Np, (Si), Fe, (Ca), Zr, (Ti), U, (Mg), (Al))

The insoluble residue, and various additions described above, were transferred to a 30-ml platinum dish with the aid of 3 ml of concentrated nitric acid; 1 ml 70% perchloric acid and 1 ml 40% hydrofluoric acid were added, and the whole was evaporated under an infra-red lamp to fuming and until only a trace of liquid remained. The heating with nitric, perchloric, and hydrofluoric acids was repeated twice, and the almost-dry residue was dissolved in 10–15 ml 6 N HNO_3, transferred to a 40-ml centrifuge tube, and made alkaline with CO_2-free concentrated ammonia or ammonia gas. The platinum dish was washed with a little CO_2-free concentrated ammonia solution to dissolve a trace of silver chloride which results from the presence of traces of chloride ion in reagents, and the washings were added to the suspension in the centrifuge tube. The precipitate was well centrifuged and the supernatant solution *C* removed. The precipitate *D* was washed with 3 ml of 2% ammonium nitrate solution and the washes were added to solution *C*. It must be added at this point that the solubilization of the insoluble residue *B* is quite a difficult step until experience has shown the correct technique. It should be stressed that the thorough washing of all precipitates added to the platinum dish aids facile dissolution with acids.

[7] W. W. SCOTT and N. H. FURMAN, *Scott's Standard Methods of Chemical Analysis*, D. Van Nostrand New York (1939).
[8] G. KAYAS, *Chim. Phys.*, **47**, 408 (1950).
[9] A. E. STEEL, *Nature*, **173**, 316 (1954).

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4. PRECIPITATE *D*
(*Containing* Zr, (Ti), U, Np, Pu, *Rare Earths*, (Fe), (Al))

The precipitate *D* was redissolved in the minimum 6 N HNO_3 and was reprecipitated with CO_2-free ammonia. The precipitate was centrifuged off and the supernatant solution was added to solution *C*; 5 drops of 5% NH_4OH . HCl solution were then stirred into the precipitate to reduce plutonium to the III-valent state, followed by 10 ml of 3 N NaOH to extract aluminium; the extraction was continued with warming on a water bath and stirring. The insoluble part was centrifuged off and re-extracted with the same quantities of hydroxylamine and caustic soda, followed by two further 4-ml aqueous washes of the insoluble part *E*.

5. TREATMENT OF SOLUTION *C*
(*Containing* Ag, Cd, Ba, Sr, (Ca), (Mg))

The ammoniacal solution was boiled down to 5 ml and acidified with a minimum of 6 N HCl, warmed to coagulate the *silver chloride* precipitate (which was then removed), and washed with 5 ml water by centrifuging, and reserved for purification.[9] The removal of ammonia from solution *C* by boiling is essential to obtain good recoveries of silver chloride, since the presence of large quantities of ammonium salts, which would be obtained by acidification, interferes with the precipitation of silver chloride; they also give rise to difficulties in the later separation of cadmium and barium, strontium, (calcium), (magnesium). The solution and washings were warmed, the acidity reduced to <0·5 N, and *cadmium sulphide* precipitated by H_2S together with a small quantity of the nickel which may have been eroded from the fusion crucible. The precipitate was washed, removed, and purified,[10] and the cadmium was finally mounted as the oxinate. The supernatant liquid was combined with the washings and evaporated to approx. 3 ml made alkaline with 1 ml conc. ammonia, an equal volume of saturated sodium carbonate solution added, and the whole boiled. The suspension was chilled and allowed to stand to complete the precipitation of *barium*, *strontium*, (*calcium*), (*magnesium*) *carbonates*, which were further purified.[10, 11]

6. INSOLUBLE PART *E*
(*Containing* Np, Pu, U, Zr, (Ti), (Fe), *Rare Earths*)

The elements contained in this precipitate were separated, using two ion-exchange columns (neptunium, plutonium, and uranium being separated as anionic complexes and the rare earths and zirconium as cationic complexes), after removal of any iron by solvent extraction.

The anion-exchange column consisted of a 5-ml burette filled between the top and bottom graduations with a bed of Deacidite-FF resin in the form of spherical granules approx. 1 mm in diameter (column length approx. 25 cm). The column was first prepared by washing with 25 ml each of the following solutions in order:

(a) 11–12 N HCl solution,
(b) Water,
(c) 11–12 N HCl containing 0·75 g NH_4I crystals in 25 ml,
(d) 2 N NaOH,
(f) Water,
(g) 11–12 N HCl.

Shortly before use, the column was washed with 50 ml 11–12 N HCl containing 0·5 ml concentrated nitric acid, and then immediately before being used the column was washed with 25 ml 9 N HCl, containing 5 drops concentrated nitric acid. Any bubbles which formed during these washes were removed by displacing the whole column in wash-liquor up into a funnel attached to the top of the column.

Insoluble part *E* was dissolved in the minimum of 8 N HCl and, if required, any $FeCl_3$ was extracted with three successive equal volumes of isopropyl ether previously saturated with 8 N HCl. The separated aqueous layer was then evaporated almost to dryness; the residue was dissolved in 10 ml 9 N HCl containing 4 drops of concentrated nitric acid to oxidize neptunium and plutonium to

[10] E. R. THOMPKINS, *J Amer. Chem. Soc.*, **70**, 3520 (1948).
[11] F. NELSON and K. A. KRAUS, *J Amer. Chem. Soc.*, **77**, 803 (1955).

the tetravalent state, and the solution was run on to the anion-exchange column, the effluent from the column being maintained at 1 drop/sec. When the level of the solution reached the top of the resin bed, 25 ml of 9 N HCl containing 5 drops concentrated nitric acid were run through the column, and the acid solutions from the column were combined and evaporated to small volume (solution *F*). *Plutonium* was removed from the anion-exchange column by elution with 25 ml 9 N HCl containing 0·75 g NH_4I. *Neptunium* was then removed from the column, by elution with 50 ml 3 N HCl solution, followed by *Uranium* on eluting with 250 ml 0·25 N HCl. After removal of the acid by evaporation, the three elements may be estimated by standard methods.

Note—If acid stronger than 9 N is used to dissolve the insoluble part *E*, some zirconium may remain on the column and elute with plutonium and neptunium. The behaviour of uranium on anion-exchange columns has been described by KRAUS and NELSON.[13]

7. SOLUTION *F*
(*Containing Rare Earths*, Zr (Ti))

Solution *F* was treated for separation of zirconium and the rare-earth elements by the method of CUNINGHAME, MERCER *et al.*[13] the zirconium (titanium) eluting from the cation exchanger column using citric or lactic acid as eluant, before any of the rare earths. Zirconium was conveniently detected in the column effluent by precipitation of the iodate from solution made strongly acid with nitric acid. The precipitate was collected and further purified from titanium by dissolution in a few drops of concentrated hydrochloric-acid and hydrogen-peroxide dilution to 6 N HCl solution, and precipitation of the zirconium as mandelate from the heated solution by addition of an equal volume of a saturated aqueous solution of mandelic acid.[14, 15] The counting data obtained on the zirconium mandelate precipitate show that niobium-daughter is removed completely by this procedure. Rare earths are eluted successively from the column, and were recovered from the numerous fractions taken by precipitation with oxalic acid. Occasionally small amounts of resin contaminated the oxalate precipitate, in which case the latter was dissolved in an oxidizing medium, the resin centrifuged off, and the oxalate reprecipitated after neutralizing the excess acid. The rare earths were mounted and weighed as the hydrated oxalate under standard conditions of preparation.

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Radiochemical Purifications

In the separation described above, the detailed procedures have been given to the point where prior publications (see references), have already described the necessary separations and radiochemical purifications. Where this work has differed from that of MEINKE,[1] in the choice of compounds for mounting and counting, the compounds used have been stated; they were chosen for ease of mounting as fine precipitates by a filtration technique, and for stoichiometric stability.

Additional Elements

So far the only other elements which have been added to the original scheme described above have been Ca, Fe, Al, Ti, Si, Mg. Some of the silicon remains in the mother-liquors from the separation of caesium and rubidium, and the rest is removed as SiF_4 during dissolution of the insoluble part *B*. Calcium and magnesium were removed along with barium and strontium, and the iron was extracted with isopropyl-ether from the HCl solution of insoluble part *E*. Aluminium was extracted as described above, titanium follows zirconium, and the activity required was separated by conventional methods.

Results

As a measure of the efficiency of the procedure, details are given in Table 1 of the mean chemical yields for elements commonly separated by twelve operators, over approximately twenty irradiations of Pu^{239} and natural uranium. These operators had previously performed two inactive practice separations. The yields quoted

[13] K. A. KRAUS and F. NELSON, International Conference on the peaceful uses of Atomic Energy, Paper No. A/CONF. 8/P/837.
[13] J. G. CUNINGHAME, M. L. SIZELAND, H. H. WILLIS, J. EAKINS, and E. R. MERCER, *J. Inorg. Nucl. Chem.*, **1**, 164 (1955).
[14] E. C. MILLS and S. E. HERMON, *Analyst*, **78**, 256 (1953).
[15] R. BELCHER, A. SYKES, and J. C. TATLOW, *Analytica Chim. Acta.*, **10**, 34-37 (1954).

naturally show the effects of the radiochemical purifications applied after the chemical separation here described, which in general were such as to produce a sample decontaminated from foreign activities by a factor of at least 10^4. In cases where

Table 1. Mean chemical yields for some typical elements after separation and radiochemical purification

Element	Ba	Sr	Mo	Ag	Cd	Zr	Ru	Y	Eu	Nd	Pr	Ce
Mean Yield	52%	46%	66%	68%	41%	42%	57%	60%	72%	73%	69%	68%

tracer quantities of plutonium and neptunium have been present in the original activity, 90% recovery or over has been obtained by careful working, with as little as 10^{-12} g of the element.

Discussion

The basic procedure described in this paper has been thoroughly tested for the separation of elements of interest in the fission of plutonium and uranium, in which not more than approx. 20 mg of the target have been irradiated or where not more than 250 mg of a rock-matrix was present. There seems to be no reason why the scheme should not be applied to moderately larger quantities of target materials if an anion-exchange column of suitable capacity were used to separate the heavy elements. Also, different targets could easily be accommodated, e.g., thorium traverses the separation procedure along with the rare earths and can be separated from them and zirconium[16] on the cation exchanger column prior to complete rare-earth separation. Radium isotopes would no doubt follow barium, strontium, and calcium, and can be separated from these elements by ion-exchange methods. If the conditions of irradiation and the aims of experiment allow it, the barium, strontium, (calcium), cadmium part of solution *C* (Fig. 1), after removal of silver, may be added to the zirconium, rare-earth fraction *F*, and the whole mixture separated on one column by successive pH changes in the citrate or lactate eluant, the cadmium eluting between lanthanum, the last rare-earth element off the column, and calcium, the first alkaline earth. Such examples may be multiplied, and other modifications to the basic scheme as here presented will depend on the results required.

Acknowledgements—The authors claim no novelty for the individual separations by ion-exchange. Acknowledgements are due to Dr. J. Milsted for much information on anion-exchange, to Dr. F. Morgan, E. R. Mercer, and Dr. R. Monk, of A.W.R.E., Aldermaston, whose experience in the analysis of complex mixtures has been made freely available.

[16] W. E. Brown and W. Rieman, *J. Amer. Chem. Soc.*, 74, 1278 (1952).

J. Inorg. Nucl. Chem., 1956, Vol. 2, pp. 229 to 236. Pergamon Press Ltd., London

ON THE STABILITIES OF TRANSITION METAL COMPLEXES—II

MAGNETIC AND THERMODYNAMIC PROPERTIES

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(*Received* 22 *December* 1955)

Abstract—The theory developed in Part I is used to discuss the magnetic criterion for bond type and the thermodynamic properties of complexes. The importance of spin-orbit coupling energies is examined. Finally, it is shown that the special properties of particular d^n complexes obtained in these two papers can be related almost entirely to exchange energies.

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1. INTRODUCTION

AN approximate theory of the energies of transition metal complexes with regular octahedral and tetrahedral symmetry was presented in Part I.[1] It was shown that a complex would have a covalent state (according to the magnetic criterion) as its lowest energy state if

$$\Delta > \Pi\,, \tag{1}$$

where Δ is the difference in energy between the two types of orbital into which the d shell is split. Π was called the mean pairing energy and is the average coulomb and exchange energy required to take an electron from an upper type of orbital and place it in a lower type. It is shown in terms of RACAH's spectral parameters in Table 1 for octahedral complexes. For a d^n tetrahedral one, the expression for Π in terms of B and C is the same as that for a d^{10-n} octahedral one.[1] Then a covalent state is

TABLE 1.—CALCULATED VALUES OF Π IN TERMS OF RACAH'S PARAMETERS AND IN CM^{-1}, FOR FIRST TRANSITION SERIES OCTAHEDRAL IONS

		M^{++}	M^{+++}
d^4	$6B + 5C$	23,520	28,000
d^5	$7\frac{1}{2}B + 5C$	25,490	30,000
d^6	$2\frac{1}{2}B + 4C$	17,620	21,000
d^7	$7B + 4C$	22,520	27,000

more stable than an ionic one because more electrons are in the lower energy type of d orbital, but less stable because the d electrons are closer together and have less exchange energy. Equation (1) represents the balance between the two.

We have already seen in Part I that no appreciable fraction of the molecules will be in a half-quenched state, so in order to decide which species should occur experimentally we need only consider the equilibrium

$$(MA_n)_i \leftrightharpoons (MA_n)_c \tag{2}$$

[1] J. S. GRIFFITH, *J. Inorg. Nucl. Chem.* **2**, 1 (1956).

between the ionic and covalent species. These two species differ only in the arrangement of electrons, and so it would seem probable that the entropy changes would not be very large. If so, then we may use the difference of the heats of formation as an estimate for the free-energy change in (2) and use (1) to determine which species is more stable. We must then also note that, in fact, a complex MA_n will not necessarily be strictly regular, in particular orbitally degenerate complexes always being expected to distort.[2] Further, in deriving (1), we have neglected the spin-orbit coupling energy. Considering all these things, we may say that we shall use (1) as a criterion for prediction only if $|\Delta - \Pi|$ is large enough—perhaps greater than 2000 cm^{-1} for the first transition series. If $|\Delta - \Pi|$ is smaller than this, then the theory in its present simple form cannot give a prediction, although for many such complexes we would expect an appreciable concentration of both forms at room temperature. Although we cannot rigorously justify the use of (1) as a theoretical criterion for bond type, it appears to give agreement with experiment for simple complexes, and so it seems reasonable to use it as it stands and then to examine more closely any complexes for which it fails.

Before applying this idea in detail we note that, for those complexes for which it is defined, Π is not even the same expression in terms of B and C for all. The coefficients are largest for d^5 complexes and smallest for d^6 octahedral and d^4 tetrahedral complexes. Thus, other things being equal, we expect the spin to be quenched most easily in the last two cases. Similarly, the total pairing energy P is much larger for d^5 ions than for the others, so we expect such covalent ions to have lower heats of formation than their neighbours (d^4 or d^6) with the same ligated groups. These expectations are discussed in more detail in Sections 2 and 4.

Finally, in discussing the relative stability of octahedral and tetrahedral complexes of the same ion, the pairing energies are important. d^5 ions have the same pairing energies for both symmetries. But d^4 and d^7 tetrahedral ions have smaller pairing energies than the corresponding octahedral ones (the d^7 tetrahedral ion has no pairing energy), and the converse is true for d^3 and d^6 ions. However, although Π makes a substantial contribution to the energies of covalent complexes, it will not necessarily be the major factor in determining the co-ordination number.

2. THE MAGNETIC CRITERION FOR BOND TYPE

We now consider, as an example, the ground states of aqueous ions of the first transition series. We assume, as generally supposed, that each such ion is surrounded octahedrally by six water molecules. Then the value of Δ is known for many of them from the interpretation of optical spectra.[3, 4] For a given ionic charge, the variation of Δ along the series is not very large, being about 8500–12,500 cm^{-1} for M^{++} ions and 17,000–21,000 cm^{-1} for M^{+++} ions. To evaluate Π we use the estimates of B and C given by CATALAN, ROHRLICH, and SHENSTONE.[5] They were obtained by considering the variation along the series of the energies of the lowest lying terms of the free ions and seem appropriate for our purpose, as we are also considering fairly low lying states of the d^n configurations. The calculated values of Π for M^{++} ions are shown in Table 1, together with estimates for M^{+++} ions for which few B

[3] H. A. JAHN and E. TELLER, *Proc. Roy. Soc.* **A161**, 220 (1937).
[3] J. OWEN, *Proc. Roy. Soc.* **A227**, 183 (1955).
[4] L. E. ORGEL, *J. Chem. Phys.* **23**, 1004 (1955).
[5] M. A. CATALAN, F. ROHRLICH, and A. G. SHENSTONE, *Proc. Roy. Soc.* **A221**, 421 (1954).

and no C were available. Δ is less than Π, with a great deal to spare, for all ions except d^6 of M^{+++}, which is the cobaltic ion. All these aqueous ions except Ni^{+++} are known, and all except Co^{+++} are ionic in agreement with the theory. Δ is not known for the cobaltic ion, but Π is at the upper end of the range of Δ found for other trivalent ions. Thus we expect the ionic and covalent states to have about the same energy, with the ionic state probably lower. Experimentally it appears that the diamagnetic and paramagnetic states probably do lie fairly close together, but that the diamagnetic state is at least 1000 cm^{-1} lower (FRIEDMAN, HUNT, PLANE, and TAUBE).[6] In view of the many approximations of the theory we could not expect a better agreement than this. By analogy with other complexes, Δ should be larger in $Co(NH_3)_6^{+++}$, which is diamagnetic, than in the aqueous ion. Δ should be smaller in CoF_6^{---}, which has a Bohr magneton number of 5·3[7] in accord with a ground-state having a total spin of 2. All these things suggest that the theory is correct in broad outline, although the exact numerical values of the quenching threshold Π given in Table 1 should only be considered accurate to within 2000 cm^{-1} or possibly more.

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The important thing about this interpretation of the diamagnetism of aqueous Co^{+++} is the light it throws upon the significance of PAULING's magnetic criterion.[7, 8] In the inequality (1), Δ is a quantity which is a mutual property of ion and ligand—it varies when either is changed. Π, however, changes only with the ion—it is the same for all complexes of a given ion. This means that, for a particular ion M^{n+}, say, Π forms a threshold above which Δ has to lie in order to quench the spin. So, for M^{n+}, the Δ for a covalent complex is larger than the Δ for an ionic complex, i.e., the influence of ligand upon ion d orbitals is greater for a covalent than for an ionic complex of the same ion. This is very close to the idea that the bonding is stronger in covalent complexes and provides a convenient theoretical background to it. However, the influence of the ligand need not be due only to chemical bonding but may be partly, at least, purely electrostatic.

When we pass along a transition series, keeping the ligands and the degree of ionization constant, the situation is different. A change of magnetic type is now more likely to reflect a change of Π than of Δ. With the M^{+++} aqueous ions we did not assume a larger Δ for Co^{+++} than for Fe^{+++}. Π was different, reflecting an intrinsic difference between the free ions, not a difference in the influence of the ligands. In particular, we have no justification from the magnetic evidence for saying that the individual bonds between Co^{+++} and water are stronger than those between Fe^{+++} and water.

We can also use equation (1) the other way round: given the magnetic type of a complex, we can give some limit to the value of Δ. Remembering the approximations of the theory, if we have a covalent complex we will expect Δ to be not less than about 2000 cm^{-1} less than Π. Thus in the diamagnetic complexes of ferrous iron, e.g., $Fe(CN)_6^{4-}$ or $Fe(dipyridyl)_3^{++}$, we expect Δ to be greater than 15,600 cm^{-1}. In these complexes π-bonding may be important, but the symmetry (especially for the ferrocyanide) is nearly that of a regular octahedron, and so each of the e and t_2 sets of levels will still be approximately degenerate. However Π may be smaller because of delocalization.

[6] H. L. FRIEDMAN, J. P. HUNT, R. A. PLANE, and H. TAUBE, *J. Amer. Chem. Soc.* 73, 4028 (1951).
[7] L. PAULING, *The Nature of the Chemical Bond*, Section 16. Oxford University Press (1940).
[8] J. S. GRIFFITH, *International Conference on Co-ordination Compounds, Amsterdam.* In the press (1955).

3. THE SPIN-ORBIT COUPLING

Thus far we have neglected the spin-orbit coupling completely, and now we try to get an idea of the order of magnitude of its effects. It introduces into the Hamiltonian an extra term

$$V = \sum_i \xi_i \boldsymbol{L}_i \,.\, \boldsymbol{S}_i \,. \tag{3}$$

Its effect within the inner shells is negligible and as before we consider only the valence electrons. V affects the energy of a complex in two ways. First it splits the ground term of the free ion, and thermodynamic heats of formation are given with respect to the ground level of this term. However our previous calculations have been referred to the centre of gravity of the ground term. Hence the difference in energy between the centre of gravity and the ground level gives an extra preparation energy. In forming a complex we break down the spin-orbit coupling, pair some of the electrons (if necessary), and then form the complex having total energy

$$E = P_1 + P + (p + \lambda\Delta) \,. \tag{4}$$

In (4) P_1 is the new preparation energy and is non-negative, P is the "electrostatic" pairing energy considered previously, and p varies smoothly along a transition series (see Part 1,[1] equation 7). Secondly, V affects the energy of the complex itself either by splitting a degenerate ground configuration or by introducing mixing with excited configurations. These second effects should be small compared with the first, especially for covalent complexes. Further, at least for the first transition series, they are comparable in magnitude to the energies of distortion of complexes into less symmetrical forms. We neglect them here and evaluate P_1.

P_1 concerns the ground term only, and hence, with Russell-Saunders coupling, V has the same matrix elements (see CONDON and SHORTLEY[9]) as

$$U = \pm(\zeta_d/2S)\, \boldsymbol{L} \,.\, \boldsymbol{S} \,, \tag{5}$$

where $\boldsymbol{L}$ and $\boldsymbol{S}$ are the total orbital and spin angular momenta and ζ_d is the term interval parameter for a single d electron. The sign in (5) is positive for a shell less than half full and negative for one more than half full. For d^5 P_1 is zero and we omit this case for the moment. Apart from d^5 we always have

$$L \geqslant S \,, \tag{6}$$

and from (5) and (6) the total spread of the ground term is

$$\chi = (L + \tfrac{1}{2})\zeta_d \,, \tag{7}$$

whence

$$\begin{aligned} P_1 \text{ (first half)} &= \tfrac{1}{2}(L+1)\zeta_d = \chi(L+1)/(2L+1), \\ P_1 \text{ (second half)} &= \tfrac{1}{2}L\zeta_d = \chi L/(2L+1), \end{aligned} \tag{8}$$

for the two halves of the series. χ is obtained from tables of atomic energy levels (MOORE,[10] values in brackets estimated from data in BACHER and GOUDSMIT[11]),

[9] E. U. CONDON and G. H. SHORTLEY, *The Theory of Atomic Spectra*, pp. 194, 209. Cambridge University Press (1953).
[10] C. E. MOORE, *Atomic Energy Levels*. Circular of the National Bureau of Standards, No. 467, Vols. 1 and 2. Washington, D.C. (1949, 1952).
[11] R. F. BACHER and S. GOUDSMIT, *Atomic Energy States*. New York: McGraw-Hill (1932).

and P_1 for the first two transition series is shown in Table 2. Sufficient data are not available for the third series, but it appears that P_1 is at least twice as large as for corresponding elements in the second series.

Table 2 shows that, although P_1 can be neglected without great error in the first series, it must be taken into account in the second and especially the third. The spin-orbit coupling energy is so large for the third series that it becomes doubtful if the present approximate treatment is even a useful first approximation there. However equation (4) may still be useful for qualitative correlation of the experimental data. This is particularly true because most of the compounds are diamagnetic and then the spin-orbit coupling energy is zero to first order.

TABLE 2.—VALUES OF P_1 FOR DIVALENT IONS OF THE FIRST AND SECOND TRANSITION SERIES

Element	P_1 (cm^{-1})	Element	P_1 (cm^{-1})
Sc	119	Y	435
Ti	241	Zr	849
V	333	Nb	1108
Cr	345	Mo	(900)
Mn	0	Tc	0
Fe	411	Ru	(1100)
Co	800	Rh	(2100)
Ni	973	Pd	(2500)
Cu	829	Ag	(1900)

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4. THERMODYNAMIC PROPERTIES OF COMPLEXES

It was pointed out by ORGEL[12] that for ionic complexes one would not expect a smooth variation of ΔH with atomic number for aqueous ions of the first transition series. This is due to the extra stabilization arising from the preferential orientation of d electrons away from the bond directions in non spherically symmetric ions. These are shown in units of Δ in Table 8 of Part 1.[1] The extra stabilization leads to an especially low value for ΔH for d^5 and d^{10} ions compared with their neighbours.

For covalent complexes, however, the calculated heat of solvation is given by $-E$ from equation (4). We have already seen that for the first transition series P_1 is small compared with the other terms, and we neglect it at first. Then $-p$ increases uniformly from d^0 to d^{10}. P, however, is zero except for d^4, d^5, d^6, and d^7 (d^3, d^4, d^5, and d^6 for tetrahedral ions) and is a maximum in either case for d^5. $\lambda\Delta$ is zero for ions up to d^6 and then increases linearly to 4Δ for d^{10}. Thus ΔH from (4) should have minima at both d^5 and d^{10}, and the general form of a plot of ΔH against atomic number should be the same either if all the complexes are ionic or if the central members of the series are covalent. We emphasize, however, that it is for an entirely different reason in the two cases.

As P_1 is always non-negative and is zero for d^0, d^5, and d^{10} ions, it works in the opposite direction and destabilizes the other ions whilst preserving the general form

[12] L. E. ORGEL, *J. Chem. Soc.* 4756 (1952).

of the curve. The experimental basis of these results has been discussed for a number of ligands by GEORGE[13] and he has noted interesting quantitative relations between the heats of solvation for different ligands.

The entropies of formation, also, would be expected not to vary smoothly along a series. For ionic complexes other than those of d^0, d^5, and d^{10} ions, the freedom of rotation of ligand molecules around the central metal ion would be restricted by the presence of d electrons in the t_2 orbitals. Thus one would expect the entropies of d^0, d^5, and d^{10} ions to be relatively higher. For covalent ions, similarly, the entropies should be relatively greatest for d^0 and d^{10} ions and relatively least for d^6 ions. However it appears experimentally that the variation of ΔS along a series is very small (see GEORGE[13]) so it may be rather difficult to test these predictions.

5. PHYSICAL SIGNIFICANCE OF THE RESULTS

Some of the results we have obtained may seem intuitively rather surprising. For whenever we quench the spin by one unit in a complex we always seem to do the same thing. We take an electron from a less stable d orbital and place it in a more stable one; and in every case the orbital which loses the electron contains no other electron whilst the orbital which receives it already contains one. Then would we not expect the pairing energy to change by practically the same amount each time, and Π to be the same for all complexes for which it is defined? But the non-existence of regular half-quenched complexes and the greater ease of quenching the spin in d^6 octahedral complexes over d^5 have been made to depend on the fact that Π is not always the same. Thus it is desirable to have a physical reason for this, not only to explain what is wrong with the argument just outlined, but also to strengthen the hope that we would obtain essentially the same results if we could remove all the approximations of our theory.

For this purpose we observe that all our d electron ground state wave functions are of a rather special kind. Each one can be expressed as a single determinant of one-electron functions. This means that, apart from a phase factor, each is completely defined when a non-ordered set of spin-orbitals for the electrons is given. For example, the d electron state in the diamagnetic cobaltic ion is given by saying that the six electrons are all in the t_2 orbital triplet, three with α spin and three with β. We now require, further, that the orbitals used in the determinants shall be the real orbitals adapted to octahedral and tetrahedral symmetry, namely $(\xi, \eta, \zeta) \in t_2$ and $(0, \varepsilon) \in e$, and we include with these the four other functions belonging to e which are identical with 0 and ε except for spatial orientation (i.e., defined with respect to the x or y axes). Then each state of $d^3, \ldots, d^7$ ions can be expressed as a single determinant of these orbitals except for the d^3 tetrahedral and d^7 octahedral ionic states. For these two there is a state of this type lying $3B$ above the ground state of the gaseous ion and in this discussion we shall consider energies relative to this.

The energy of a single determinant function can be written in the form

$$E = J - K, \tag{9}$$

where J is the coulombic energy and K the exchange energy. In general J and K depend upon the choice of orbitals in the determinant but we have restricted the

[12] P. GEORGE, *International Conference on Co-ordination Compounds*, Amsterdam. In the press (1955).

possible orbitals so much that J and K are now uniquely defined in terms of the total wave function. Then we can also split the pairing energy P into two parts P_c and P_e, where P_c is the increase in coulomb energy consequent upon quenching the spin and P_e is the decrease in the positive exchange term K. Similarly we can split Π giving

$$P = P_c + P_e, \qquad \Pi = \Pi_c + \Pi_e. \tag{10}$$

Π_c and Π_e are shown in Table 3. As B is much smaller than C, we see that our somewhat classical argument about the constancy of Π does apply to Π_c but not at all to Π_e. Π_e is a consequence of destroying exchange energy and for a determinant

TABLE 3.—THE COULOMB AND EXCHANGE PARTS OF THE MEAN PAIRING ENERGY.

		Π_e		Π_c		Π_c/D	
Tetra-hedral	Octa-hedral	half-quenched	covalent	half-quenched	covalent	half-quenched	covalent
d^6	d^4	—	$2C$	—	$6B + 3C$	—	$2B + C$
d^5	d^5	$2C$	$B + 2C$	$10B + 4C$	$6\frac{1}{2}B + 3C$	$2\frac{1}{2}B + C$	$2\frac{1}{2}B + C$
d^4	d^6	$-2B + 2C$	$-B + 2C$	$7B + 3C$	$3\frac{1}{2}B + 2C$	$2\frac{1}{2}B + C$	$1\frac{1}{2}B + C$
d^3	d^7	—	$2C$	—	$4B + 2C$	—	$2B + C$

having m electrons with α spin and n with β spin the number of non zero terms making up K in (9) is

$$N(m, n) = \tfrac{1}{2}m(m-1) + \tfrac{1}{2}n(n-1). \tag{11}$$

From (11) we can calculate the average decrease D of N per unit of spin quenched in forming a complex. The ratios of Π_e to D are also shown in Table 3. The fact that Π_e and Π_e/D vary very little suggests that a simple model in which the coulomb energy changes by a fixed amount $2C$ each time the spin is quenched one unit and in which the exchange energy K is proportional to $(2B + C)N$ would have fair quantitative agreement with the more complete treatment of Part I. In fact the error in Π through using such a model is never more than $2B$ (as mentioned before, we must subtract $3B$ for the energy of a gaseous ion for d^3 and d^7).

It may be fortuitous that the simple model works so well, nevertheless the analysis presented in this section is interesting because it seems to expose the reason lying behind our results. The mean pairing energies differ from one another because the amount of exchange energy which is destroyed differs. And this is something which, although it has a precise meaning only in terms of a chosen set of orbital functions, appears to have a rather general significance. It finds its expression in the field of atomic spectra in HUND's rule for determining the spin of the ground state of an atom. Then we may feel that the theory rests on a physical basis which is more general than the approximations in the quantum mechanics and the assumptions about the nature of the complexes, used in these papers, might suggest.

Since completion of this work, it has come to my notice that some of these results have been obtained by Dr. L. E. ORGEL.[14] It still seems worth while, nevertheless, to publish the present paper, as the approach is somewhat different from Dr. ORGEL's, and the paper contains results not obtained by him.

Acknowledgements—The author wishes to express his gratitude to Professor P. GEORGE, whose enthusiasm for the thermodynamics of transition metal complexes was mainly responsible for the instigation of this work, and to Professor H. C. LONGUET-HIGGINS for his comments on the paper.

[14] L. E. ORGEL, *J. Chem. Phys.* **23**, 1819 (1955).

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NITROGEN BOND STRAIN EFFECTS IN THE CHEMISTRY OF RING-AMINO BORON HYDRIDES

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(*Received* 25 *November* 1955)

Abstract—Compounds of the types $(R_2NBH_2)_2$ and $R_2NB_2H_5$ are fairly stable even though the B—N—B bond angles are far less than tetrahedral; however, when the N bonds are further strained, as in the ring-amino boron hydrides $(C_3H_6NBH_2)_2$ and $C_3H_6NB_2H_5$, the result is instability. Attempts to make the still more N-strained $(C_2H_4NBH_2)_2$ and $C_2H_4NB_2H_5$ lead instead to opened-ring products. The full comparison has included synthesis of the new compounds $C_5H_{10}NBH_2$ (assoc.; m.p. 110°; b.p. est. 202°), $C_5H_{10}NB_2H_5$ (liquid; b.p. est. 148°), $C_4H_8NBH_2$ (assoc.; m.p. 34°; b.p. est. 194°), $C_4H_8NB_2H_5$ (m.p. −63·5°; b.p. est. 122°), $(C_3H_6NBH_2)_2$ (m.p. 51·8°; b.p. est. 186°), $C_3H_6NB_2H_5$ (m.p. −45·4°; b.p. est. 101°), $C_2H_5NHB_2H_5$ (m.p. −96·4°; b.p. est. 87°), and n-$C_3H_7NHB_2H_5$ (glass softening −146 to −142°; b.p. est. 121°). The corresponding N—BH_3 complexes were observed; and the mono-strained $C_2H_4NH \cdot BH_3$ proved to be fairly stable.

THE relatively high stability of dimethylaminodiborane, $(CH_3)_2NB_2H_5$,[1] wherein the B—N—B bond angle is 76° and C—N—C nearly 112°,[2] implies the possible existence of many other aminodiboranes, including some in which the C—N—C angle would be relatively fixed by inclusion in a ring. In piperidinodiborane ($C_5H_{10}NB_2H_5$) the C—N—C angle could easily adjust toward 112°, permitting the aminodiborane part to have the same geometry and high stability as dimethylaminodiborane; and pyrrolidinodiborane ($C_4H_8NB_2H_5$) should conform well enough for similar stability. Also the corresponding aminoborines $C_5H_{10}NBH_2$ and $C_4H_8NBH_2$ should exhibit association equilibria similar to the monomer-dimer status of $(CH_3)_2NBH_2$.[3] These compounds now have been made in virtually quantitative yields, and their properties are consistent with all expectations.

Similar compounds derived from azetidine (C_3H_6NH) should be less stable because the N bond strain due to small B—N—B angles would be supplemented by the restricted C—N—C angle, which surely could not much exceed 90° even though the B—N—B strain would require some widening. Thus the double strain on N in a $(BN)_2$-ring dimer of $C_3H_6NBH_2$ could mean that some other kind of polymerization would be preferred, and in $C_3H_6NB_2H_5$ the low C—N—C angle might so work against the stability of the NB_2H bridge as to promote the loss of BH_3 as diborane.

Actually, the dimer of $C_3H_6NBH_2$ was obtained as a volatile solid by the protolysis of the adduct $C_3H_6NH \cdot BH_3$, and its further conversion to $C_3H_6NB_2H_5$ by absorption of diborane was virtually quantitative. However, the yield of $(C_3H_6NBH_2)_2$ never exceeded 40%, the major product being a nonvolatile glassy material having the same average composition, but incapable of absorbing diborane. An apparently similar material was formed when $C_3H_6NB_2H_5$ irreversibly decomposed with evolution of diborane. A higher polymer of $C_3H_6NBH_2$ would represent an alternative to the

[1] A. B. BURG and C. L. RANDOLPH, JR., *J. Amer. Chem. Soc.* **71**, 3451 (1949).
[2] K. HEDBERG and A. J. STOSICK, *ibid.* **74**, 954 (1952).
[3] A. B. BURG and C. L. RANDOLPH, JR., *ibid.* **73**, 953 (1951).

double strains on N in $(C_3H_6NBH_2)_2$ and $C_3H_6NB_2H_5$, but it has not been decided whether the glassy product was a $(—B—N—)_n$ higher polymer, or a result of opening the C_3N ring.

The unusually high strain on N in ethylenimine leads to ring opening when one attempts to add to the strain by making $C_2H_4NB_2H_5$. Neither this nor any form of $C_2H_4NBH_2$ could be prepared; instead, the action of diborane upon the fairly stable $C_2H_4NH \cdot BH_3$ gave a fair yield of the new compound $C_2H_5NHB_2H_5$, and there were indications of the alternate products $(C_2H_5NBH)_3$ and polymeric $C_2H_5NHBH_2$. The results thus bear some analogy to the behaviour of diborane toward alkene oxides.[4]

EXPERIMENTAL

Preparation and Characterization of Reagents

Piperidine and pyrrolidine—Commercial samples were purified by contact with potassium hydroxide and high-vacuum fractional distillation (including the use of a wire-spiral microcolumn) until tensiometric uniformity was observed. Middle fractions were used for determining the vapour tensions shown in Tables 1 and 2. For piperidine, the values determined the equation $\log p_{mm} = -(2533/T) + 1{\cdot}75 \log T - 0{\cdot}00746T + 7{\cdot}866$, from which the normal boiling-point is 105·3° (literature, 106·3°) and the Trouton constant is near 20·4 cal/deg mole. For pyrrolidine, the equation is $\log p_{mm} = -(2486/T) + 1{\cdot}75 \log T - 0{\cdot}00836T + 8{\cdot}302$; b.p. 88·4° (literature, 88·5°) and Trouton constant 20·7.

TABLE 1.—VAPOUR TENSIONS OF PIPERIDINE

t (°C)	15·0	19·2	24·5	27·1	33·5	46·3	54·6	61·9
p_{mm} (obsd)	16·9	21·6	29·4	33·4	46·5	86·7	124·4	168
p_{mm} (calcd)	17·0	21·7	29·1	33·5	46·8	86·2	124·4	167

TABLE 2.—VAPOUR TENSIONS OF PYRROLIDINE

t (°C)	−15·36	5·95	9·66	16·09	22·38	29·18	37·35
p_{mm} (obsd)	5·29	22·1	27·4	39·4	55·2	78·3	115·1
p_{mm} (calcd)	5·29	22·0	27·4	39·5	55·3	78·2	115·1

Azetidine—In the absence of a commercial sample of azetidine, the corresponding amide was prepared from *p*-toluenesulphonamide and 1,3-dibromopropane[5] and treated with sodium in liquid ammonia. The fast reduction yielded azetidine, which was isolated by distilling off the ammonia and subjecting the residue to high-vacuum distillation in a microcolumn having a reflux temperature of −65°. In this process a fraction having the volatility of toluene was eliminated. The yield of the desired C_3H_6NH ran as high as 30% of the N,N-trimethylene-*p*-toluenesulphonamide, and the procedure was more convenient than the previously-employed reduction by sodium in *n*-pentanol. The vapour tensions, represented in Table 3, determine the equation $\log p_{mm} = -(1849/T) + 1{\cdot}75 \log T - 0{\cdot}00305T + 5{\cdot}025$, from which the normal boiling-point is computed to be 60·5°, consistent with the literature.[6] The Trouton constant has the fairly high value 23·6 cal/deg mole.

Ethylenimine—Ethanolammonium acid sulphate was heated with alcoholic potassium hydroxide to form ethylenimine,[7] which was distilled off and dried over anhydrous potassium hydroxide. The

[4] F. G. A. STONE and H. J. EMELÉUS, *J. Chem. Soc.* 2755 (1950).
[5] W. MARCKWALD and A. DROSTE-HUELSHOFF, *Ber.* **31**, 3264 (1898); C. C. HOWARD and W. MARCKWALD *ibid.* **32**, 2032 (1899).
[6] H. C. BROWN and M. GERSTEIN, *J. Amer. Chem. Soc.* **72**, 2927 (1950).
[7] H. WENKER, *ibid.* **57**, 2328 (1935).

TABLE 3.—VAPOUR TENSIONS OF AZETIDINE

t (°C)	−51·0	−27·4	−16·3	0·00	7·2	11·8	17·7	19·0
p_{mm} (obsd)	1·36	8·5	18·0	48·9	72·3	91·4	124·8	132·5
p_{mm} (calcd)	1·35	8·6	18·2	48·6	72·2	91·6	123·7	131·8

product was further purified by means of a high-vacuum microcolumn having a reflux temperature of −65°. A sample of this product was stored at room temperature for two years, in contact only with glass and mercury, with no more than a 15% loss through polymerization. The vapour tensions of three freshly refractionated samples were measured, with results (shown in Table 4) which determine the equation $\log p_{mm} = -(1896/T) + 1{\cdot}75 \log T - 0{\cdot}003558T + 5{\cdot}4164$. This would mean a normal boiling-point of 55·4° (literature, 54·8° at 746 mm)[6] and a Trouton constant near 24·1 cal/deg mole. The deviations of the lowest pressures, from an equation which correlates the others, probably is a real effect not predictable by this type of extrapolation.

TABLE 4.—VAPOUR TENSIONS OF ETHYLENIMINE

t (°C)	−51	−32	0·00	4·00	9·65	16·05	20·55	45·6
p_{mm} (obsd)	1·2	6·6	58·5	73·2	99·5	137·2	171·5	519
p_{mm} (calcd)	1·6	7·2	58·5	73·2	99·1	137·6	171·7	519

Piperidine and Diborane

Piperidine borine—A 51·6-mg (13·58-cm³)[6] sample of $C_5H_{10}NH$ and 6·92 cm³ of B_2H_6 were brought together in an immersible tensimeter,[9] and after the pressure had diminished to a limit, the recovery of B_2H_6 was 0·19 cm³. The empirical formula thus was essentially $C_5H_{10}NH \cdot BH_3$. The product had a vapour tension of 0·6 mm at 40°, but a full curve was not obtained on account of the ease of incipient evolution of hydrogen.

Piperidinoborine—The $C_5H_{10}NH \cdot BH_3$ was heated for 6 h at 110–115° (yielding two-thirds of the expected hydrogen), and then for 10h at 135–45°, bringing the total evolved hydrogen to 13·38 cm³, or 98·5% of the theoretical. The resulting $C_5H_{10}NBH_2$ melted in the range 106-110°. Its vapour tensions, given by Tables 5 and 6, determine the equation $\log p_{mm} = 13{\cdot}131 - 4584/T$ for the solid and $\log p_{mm} = 9{\cdot}967 - 3368/T$ for the liquid. The normal boiling-point thus would be 202°, the molar heat of fusion 5·57 kcal, and the m.p. 111°. The high Trouton constant, 32·4 cal/deg mole, accords with the expectation of a monomer-dimer equilibrium like that of $(CH_3)_2NBH_2$.[3]

TABLE 5.—VAPOUR TENSIONS OF SOLID $C_5H_{10}NBH_2$

t(°C)	68·8	80·0	85·9	97·2	103·2	106·9
p_{mm} (obsd)	0·53	1·37	2·31	5·68	8·94	11·58
p_{mm} (calcd)	0·53	1·42	2·31	5·66	8·94	11·76

TABLE 6.—VAPOUR TENSIONS OF LIQUID $C_5H_{10}NBH_2$

t (°C)	114·9	120·4	124·3	129·8	139·3	142·1
p_{mm} (obsd)	19·4	25·7	31·0	40·8	63·6	70·5
p_{mm} (calcd)	19·4	25·6	31·1	40·6	63·3	71·0

[6] Throughout this paper the abbreviation cm³ refers to the volume which the substance would occupy as a gas at standard conditions.

[9] A. B. BURG and H. I. SCHLESINGER, *J. Amer. Chem. Soc.* **59**, 785 (1937).

Piperidinodiborane—The same sample of $C_5H_{10}NBH_2$ was treated with 6·88 cm³ of B_2H_6 at 85-100° for a little more than an hour, with occasional cooling to room temperature for observation of the formation of a liquid phase. Hydrogen now was measured as 0·12 cm³ (total now 13·47 cm³), and the recovered B_2H_6 amounted to 0·12 cm³. Hence in the overall reaction, 13·49 cm³ of B_2H_6 reacted with 13·58 cm³ of $C_5H_{10}NH$ to form 13·47 cm³ of H_2 and an equivalent volume of $C_5H_{10}NB_2H_5$. After purification by high-vacuum fractional condensation, with a slight sacrifice of yield, the product actually was measured as 12·88 cm³, confirming the quantitative synthesis. The molecular weight was determined as 109·5 (calcd. 110·8) and the regionally-averaged vapour tensions were as shown in Table 7. These determine the equation $\log p_{mm} = -(2410/T) + 1{\cdot}75 \log T - 0{\cdot}00510T + 6{\cdot}1606$, according to which the normal boiling-point would be 148° and the Trouton constant approximately 19·6 cal/deg mole.

TABLE 7.—VAPOUR TENSIONS OF $C_5H_{10}NB_2H_5$

t (°C)	24·73	35·23	40·73	49·20	56·82	64·70	71·68
p_{mm} (obsd)	7·60	13·37	17·88	26·92	38·2	53·4	71·4
p_{mm} (calcd)	7·60	13·44	17·84	26·92	38·1	53·7	71·4

Although the tensiometric behaviour of the piperidinodiborane was as expected for a pure aminodiborane type of compound, it is not necessarily true that its molecules were all of the same species, for the piperidine ring has two shapes, in one of which the N atom can have either a symmetric or *d* and *l* asymmetric positions. The resolution of the expected geometric isomers of piperidinodiborane, and an evaluation of their relative stabilities, would be interesting but very difficult.

Pyrrolidine and Diborane

Pyrrolidinoborine—A 33·3 cm³ sample of C_4H_8NH absorbed 16·46 cm³ of a 17·0 cm³ sample of B_2H_6, as the mixture warmed from −78° and melted near room temperature. The indicated complex $C_4H_8NH \cdot BH_3$ was not further characterized, but was heated at 120–135° during 2·5 h, yielding 33·7 cm³ of H_2 (calcd. 33·3). The product thus had the empirical formula $C_4H_8NBH_2$. It melted at 33·8–34·2°, and its vapour tensions, shown in Table 8, determined the equation $\log p_{mm} = 8{\cdot}675 - 2705/T$; b.p. 194° and Trouton constant 26·5 cal/deg mole. Such a high value for the Trouton constant suggests association, but the equilibrium evidently is somewhat different from that of piperidinoborine.

TABLE 8.—VAPOUR TENSIONS OF LIQUID $C_4H_8NBH_2$

t (°C)	75·6	86·9₂	92·4	104·2	111·4	124·9
p_{mm} (obsd)	8·36	14·46	18·76	31·5	43·4	75·8
p_{mm} (calcd)	8·25	14·46	18·74	31·9	43·5	75·3

Pyrrolidinodiborane—The 33·7 cm³ sample of $C_4H_8NBH_2$ absorbed 17·0 cm³ from a 17·7-cm³ sample of B_2H_6 (during 3h at 90-110°), in accord with the equation $2C_4H_8NBH_2 + B_2H_6 \rightarrow 2C_4H_8NB_2H_5$. After purification by high-vacuum fractional condensation (−26 to −31°), the product melted at −63·4 or −63·6°; average, −63·5°. Its molecular weight was determined as 96·0 (calcd. 96·8). The vapour tensions, shown in Table 9, determine the equation $\log p_{mm} = -(2205/T) + 1{\cdot}75 \log T - 0{\cdot}004539T + 5{\cdot}7217$, according to which the normal boiling-point is 121·8° and the Trouton constant approximately 20·6 cal/deg mole.

TABLE 9.—VAPOUR TENSIONS OF $C_4H_8NB_2H_5$

t (°C)	2·80	11·43	18·40	26·95	41·23	53·85	60·55
p_{mm} (obsd)	5·69	9·45	14·03	22·16	45·09	78·53	103·6
p_{mm} (calcd)	5·63	9·46	14·09	22·13	44·82	78·53	103·6

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Azetidine and Diborane

Azetidine borine—A 12·24-cm³ sample of C_3H_6NH absorbed 6·33 cm³ from a 7·17-cm³ sample of diborane, at a temperature near −60°. After warming to room temperature, the noncondensable gas was measured as 0·066 cm³. Thus the formation of $C_3H_6NH \cdot BH_3$ was quantitative. The product was observed to be a liquid at room temperature, but it was not further characterized.

Azetidinoborine—A sample of $C_3H_6NH \cdot BH_3$ was made from 9·07 cm³ of azetidine and heated for 16 h in a sealed tube at 112°, yielding 8·87 cm³ of H_2. Three products (all colourless) were observed—a solid and a liquid which were not volatile at 50°, and a 40% yield of a volatile solid which was later shown to have the composition $C_3H_6NBH_2$. Hence the nonvolatile products must have had the same average composition; however, an attempt to recover azetidine from them by aminolytic methods did not succeed, nor was it possible to obtain from them any $C_3H_6NB_3H_6$ (q.v.) by treatment with diborane. The question whether these evidently polymeric materials were formed by ring-opening reactions has not been decided.

The vapour tensions of the volatile product, shown in Tables 10 and 11, determined the equation $\log p_{mm} = 11{\cdot}811 - 3544/T$ for the solid and $\log p_{mm} = 8{\cdot}503 - 2469/T$ for the liquid. The molar heat of fusion is calculated as 4·92 kcal and the m.p. as 51·8° (obsd., 51·5–51·7°). The Trouton constant was calculated as 25·7 cal/deg mole.

The normal b.p. undoubtedly is higher than the value implied by the vapour-tension equation for the liquid; a reasonable estimate, based upon a normal Trouton constant of 21, would give the b.p. as 186°. This value probably cannot be directly observed, for the substance showed signs of instability at 70°, tending to develop traces of a far less volatile liquid. Determinations of the molecular weight of the vapour (69°, 14 mm) gave the values 134 and 136; calcd. for $(C_3H_6NBH_2)_2$, 137·8. Thus the substance evidently exists almost wholly in the form of the dimer.

TABLE 10.—VAPOUR TENSIONS OF SOLID $(C_3H_6NBH_2)_2$

t (°C)	24·3	27·3	34·0	42·2	48·0
p_{mm} (obsd)	0·79	1·05	1·85	3·74	5·98
p_{mm} (calcd)	0·79	1·04	1·87	3·74	5·97

TABLE 11.—VAPOUR TENSIONS OF LIQUID $(C_3H_6NBH_2)_2$

t(°C)	52·5	56·9	66·5	70·5	76·2
p_{mm} (obsd)	8·34	10·47	16·95	20·6	27·8
p_{mm} (calcd)	8·34	10·54	17·14	20·8	27·3

Initial preparation of azetidinodiborane—The first preparation of $C_3H_6NB_3H_5$ was from the 12·24-cm³ sample of $C_3H_6NH \cdot BH_3$. This was heated for 9 h at 100–110° to yield the typical mixture of nonvolatile solid and liquid and volatile solid; the yield of hydrogen was near the calculated value, but was not accurately measured. The mixed product was repeatedly heated with diborane in the immersible tensimeter[9] at temperatures near 100°, with frequent removal of the desired product—a liquid which could be distinguished by its vapour tension of 11 mm at 0°, after passing a U-trap at −40° and condensing at −55° under high vacuum. The yield asymptotically approached 4·5 cm³ (37%) at the cost of 3·02 cm³ of B_2H_6. The volatile solid was used up, but the nonvolatile components seemed to be unaffected.

Proof of the formula $C_3H_6NB_3H_5$—A 4·47-cm³ sample of the purified product had a weight of 16·0 mg, implying that the molecular weight was 81·6 ± 1 (calcd. for $C_3H_6NB_3H_5$, 82·8). A 2·86-cm³ sample was hydrolysed at 100°, in the presence of 2·86 cm³ of HCl, yielding 13·96 cm³ of H_2 (calcd. 14·3). The resulting aqueous solution was neutral to methyl red, showing that the HCl had been neutralized by one mole of amine per mole of the original sample. The boric-acid titration gave 0·265 mmole of B, equivalent to 2·08 B atoms per molecule. Taken with the molecular weight, these analytical results left no doubt of an aminodiborane at least close to the formula $C_3H_6NB_3H_5$; and

the conditions of synthesis would indicate that the azetidine ring remained unbroken. However, to make sure of this point, n-$C_3H_7NHB_2H_5$ was synthesized (as described in a later section), and shown to have very different physical properties.

Improved preparation of azetidinodiborane—A more efficient production of $C_3H_6NB_2H_5$ was managed by heating the liquid complex $C_3H_6NH \cdot BH_3$ in the lower tube-end of an immersible tensimeter[9] containing diborane at an initial pressure of 0·35 atm. The tube-end was immersed, just to the level of the inner liquid, in an oil-bath at 150-180°, so that a convection-stream of diborane could pick up $C_3H_6NBH_2$ units as fast as they were formed by loss of hydrogen from the complex. At frequent intervals the hydrogen was pumped off for measurement and the desired $C_3H_6NB_2H_5$ was isolated; then the hot contact between the remaining diborane and the decomposing complex was repeated. In this manner it was practicable to convert 34·9 cm³ of C_3H_6NH to 27·6 cm³ (79% yield) of $C_3H_6NB_2H_5$, with formation of 34·9 cm³ of H_2 and use of 31·2 cm³ of B_2H_6. According to these quantities, the virtually inactive nonvolatile residue again had the average composition $C_3H_6NBH_2$.

Characterization of azetidinodiborane—The m.p. of $C_3H_6NB_2H_5$ was determined by direct observation, as −45·4°. Its vapour tensions, shown in Table 12, determine the equation $\log p_{mm} = -(2248/T) + 1{\cdot}75 \log T - 0{\cdot}00616T + 6{\cdot}6928$, according to which the normal b.p. would be 101° and the Trouton constant 20·2 cal/deg mole. The instability of this substance was indicated by an increase of its vapour tension at 0° from 11 to 13 mm during two days at room temperature; and a 3·70-cm³ sample, after three months in a sealed tube at room temperature, yielded 0·14 cm³ of B_2H_6 and a nonvolatile colourless gummy liquid. The recovery of $C_3H_6NB_2H_5$ was 3·10 cm³, or 84%.

TABLE 12.—VAPOUR TENSIONS OF AZETIDINODIBORANE

t (°C)	−30·2	−13·5	−4·8	0·00	4·8	13·6	23·6	33·0
p_{mm} (obsd)	1·34	4·57	8·24	11·01	14·83	24·50	41·34	65·32
mm (calcd)	1·31	4·58	8·17	11·07	14·79	24·42	41·34	65·27

Synthetic proof of the formula $(C_3H_6NBH_2)_2$—The previously-mentioned volatile solid decomposition product of the azetidine borine complex was converted according to the equation $(C_3H_6NBH_2)_2 + B_2H_6 \rightarrow 2C_3H_6NB_2H_5$ in a virtually quantitative experiment serving as proof of the formula $(C_3H_6NBH_2)_2$. A 5·0-mg sample, measured as 0·84 cm³ of standard gas, was treated repeatedly with diborane (initially 4·11 cm³) in a space of 70ml at 90-98°, with frequent removal of the resulting $C_3H_6NB_2H_5$, until no more of this could be obtained, and no more of the solid azetidinoborine could be detected. The total yield of $C_3H_6NB_2H_5$ (m.p. −45·3°; vapour tension 11·2 mm at 0°) was 1·52 cm³, or 95%. The apparent use of diborane was 1·11 cm³, including the possibility of slight decomposition.

Synthesis of propylaminodiborane for comparison—A ring-opening reaction of azetidine with diborane would place H on C and B on N, leading to (n-$C_3H_7NHBH_2$) and n-$C_3H_7NHB_2H_5$. Had this happened in the foregoing experiments, the supposed azetidinodiborane would have proved to be identical with samples of n-propylaminodiborane made by a direct method. Actually the azetidine and n-propylamine products showed very different physical properties.

The preparation of n-$C_3H_7NHB_2H_5$ was done by essentially the same method as previously employed for methylaminodiborane:[11] a 51·2-cm³ sample of the solid complex n-$C_3H_7NH_2 \cdot BH_3$ was prepared and heated at 100°, while 2·5 litres of diborane streamed over it at a moderate pressure.

The resulting H_2 was measured as 39 cm³. The liquid product was purified by high-vacuum fractional condensation (through −40°; trapped at −60°); the 70% yield (ca. 35 cm³) could have been increased. The apparent molecular weight of the saturated vapour was 88·5 (calcd. 84·8). Hydrolysis of a 3·3-cm³ sample (with 4 cm³ of HCl) gave 16·6 cm³ of H_2 (5·03 per mole), and a titration of the remaining HCl showed 3·5 cm³ of amine. The boric-acid titration ran high: 2·3 B per mole.

The pure n-$C_3H_7NHB_2H_5$ formed a glass which became fluid enough in the range −146 to −143° to release a frozen-on plunger. The structural similarity to 2-methylpentane (m.p. near −160°) is interesting in this connection. The 100° difference of melting point would be enough to demonstrate that the azetidine product was a different substance, but as a double check a vapour-tension curve was obtained (Table 13), showing a considerably lower volatility. The corresponding equation is $\log p_{mm} = 8{\cdot}537 - 2117/T$. The high value which this gives for the Trouton constant (25·9 cal/deg mole) implies that it would predict too low a value for the normal boiling-point; however, a line drawn from the top point of the log p vs. $1/T$ graph, with a slope corresponding to a Trouton constant of 21, gives a fairly dependable extrapolation to 121° for 760 mm.

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TABLE 13.—VAPOUR TENSIONS OF n-PROPYLAMINODIBORANE

t (°C)	−22·8	−14·1	−8·7	0·00	6·45	11·63	16·03
p_{mm} (obsd)	1·32	2·34	3·40	6·14	9·24	12·73	16·44
p_{mm} (calcd)	1·21	2·32	3·41	6·13	9·25	12·70	16·48

The instability of n-propylaminodiborane is about as expected for a primary-amino-diborane: a decomposition rate of 1·2% during four days at 25°—as measured by the production of diborane.

Ethylenimine and Diborane

The borine complex—The addition of diborane to ethylenimine, to form the complex $C_2H_4NH \cdot BH_3$, requires unusual precautions to avoid secondary or side reactions, such that the hydrolysis of the product yields less than $3H_2$ per absorbed BH_3 group. In eight experiments wherein diborane was allowed to react with a little less than twice its volume of ethylenimine, either at −78° or during free warming from −196° toward room temperature, the results of acid-hydrolysis of the non-volatile products ranged from 2·26 to 2·94 H_2 per BH_3 used. The failure to complete the kind of ring-opening reaction whereby the hydridic hydrogen would have fallen to $2H_2$ per B, should be ascribed mostly to a persistence of the $C_2H_4NH \cdot BH_3$ complex, but there could be some formation of a (—C—C—N—) chain polymer, with BH_3 on each N. In this relation it is possibly of interest that adduct samples which were not warmed above −78°, except at the end of the hydrolysis reaction, gave 2·57 to 2·76 H_2 per B, whereas more-roughly-formed samples which were heated for 15 min at 60 or 90° hydrolysed to give 2·94 or 2·51 H_2 per B, respectively.

In still another experiment, the adduct formed from 26·97 cm³ of C_2H_4NH and 13·15 cm³ of B_2H_6 was heated for 14 h at 80–90°, yielding 26·37 cm³ of H_2 and a slightly volatile liquid amounting to about 4·5 cm³ of standard gas. Its vapour tensions (e.g., 2·43 mm at 39·4°, 3·87 mm at 49·2°, and 9·01 mm at 66·4°) conformed

to the equation $\log p_{mm} = 7{\cdot}646 - 2273/T$ well enough to indicate purity, but the substance was not further characterized nor analysed. The observed loss of hydrogen could be due either to the formation of $=NBH_2$ units along a (—C—C—N—) chain, or to the formation of triethylborazole, $(C_2H_5NBH)_3$ from $(C_2H_5NHBH_2)_x$. However, the liquid was less volatile than triethylborazole.[10]

Adequate control of the complex-forming reaction was achieved by using diethyl ether as a solvent and working at lower initial temperatures. In one case 36·0 cm³ of C_2H_4NH and 20·8 cm³ of B_2H_6 were condensed into a reaction tube, overlaid by 2 ml of strictly dry ether, and warmed from −135 to −60° during 3 h. The ether was distilled off, and the excess diborane recovered from it, leaving the composition $C_2H_4NH \cdot 1{\cdot}014BH_3$. The wholly solid product (m.p. near 40°) was virtually non-volatile at room temperature, but during 3 h under high vacuum at 30° it delivered a trace of sublimate into an adjacent trap at −196°. For hydrolysis, the whole sample was submerged in ether; then water and HCl (75·0 cm³) were distilled in successively and the system was slowly warmed to 0°. The resulting hydrogen was measured as 108·0 cm³, or 2·98 H_2 per BH_3 absorbed. Titration of the excess HCl (9·3 cm³) now showed that 65·7 cm³ of it had been used; since only 36·0 cm³ would have been needed for neutralization of the amine, the extra 29·7 cm³ of HCl must have been used for opening 82·5% of the ethylenimine rings to form $ClC_2H_4NH_2$. This result indicates 17·5% as an upper limit of $(—C—C—N—)_x$ chain building, but it may have been less, since some hydrolytic ring-opening to form $HOC_2H_4NH_2$ could account for the use of less than 2·00 moles of HCl per mole of C_2H_4NH. At least the major part of the sample must have retained an intact ethylenimine ring, capable of opening under attack by HCl.

Evidence of the persistence of the C_2N ring in $C_2H_4NH \cdot BH_3$ even at 100° is to be found at the end of the following section.

Ethylaminodiborane from ethylenimine and diborane—All attempts to prepare ethyleniminodiborane ($C_2H_4NB_2H_5$) from ethylenimine and diborane yielded ethylaminodiborane ($C_2H_5NHB_2H_5$), which was easily purified and found to be physically identical to ethylaminodiborane prepared from ethylamine and diborane. Any trace of $C_2H_4NB_2H_5$ should have affected the vapour tensions or the melting-point, or both. Evidently the C_2N ring, although fairly stable in the complex $C_2H_4NH \cdot BH_3$, cannot withstand the further strain upon N which would occur in the HB_2N bridge.

In one experiment, 99·4 cm³ of C_2H_4NH and 108·2 cm³ of B_2H_6 were allowed to react at a low temperature and then heated in a sealed tube at 90° for 90 min, producing 25·1 cm³ of a substance later proved to be $C_2H_5NHB_2H_5$, but there was only 16·9 cm³ of H_2 (proved by Cu-O combustion); and the recovery of B_2H_6 was 36·0 cm³. From these results the white glassy solid by-product could be interpreted as a mixture of (—C—C—N—) polymeric $(C_2H_4NB_2H_5)_x$ involving 16·9 cm³ of the original C_2H_4NH, with (—N—B—) polymeric $(C_2H_5NHBH_2)_y$ corresponding to about 60 cm³ of monomer. The volatile aminodiborane was purified by fractional condensation (passed −46° and trapped at −78°); melting-points were determined as −96·5, −96·5, and −96·3° (avg. −96·4°) and molecular weights as 69·8, 69·9, and 72·1 (avg. 70·6; calcd. for $C_2H_5NHB_2H_5$, 70·7). Table 14 shows representative

[10] W. V. HOUGH, G. W. SCHAEFFER, M. DZURUS, and A. C. STEWART, *ibid.* 77, 865 (1955).

vapour tensions, determining the equation $\log p_{mm} = -(2096{\cdot}3/T) + 1{\cdot}75 \log T - 0{\cdot}00533T + 6{\cdot}15245$. This indicates the normal boiling-point to be 86·6° and the Trouton constant near 21·0 cal/deg mole.

TABLE 14.—VAPOUR TENSIONS OF ETHYLAMINODIBORANE

t (°C)	−38·04	−25·58	−12·24	0·00	4·95	15·05	30·06
p_{mm} (obsd)	1·37	3·58	8·91	19·31	25·70	44·28	92·41
p_{mm} (calcd)	1·36	3·59	9·04	19·32	25·70	44·35	92·42

In another experiment, the plan was to form ethyleniminodiborane by a flow method, if possible, and whisk it into a trap at −196° before the ring could open. Samples of C_2H_4NH (28·75 cm³) and B_2H_6 (26·70 cm³) were brought together in ether, warming overnight from −140° to −78°. The recovery of B_2H_6 was 14·5 cm³, implying that the $C_2H_4NH \cdot BH_3$ complex amounted to 29·0 cm³. The product was a somewhat translucent but cleanly crystalline solid which melted in the range 39–42°. It was heated to 100° under a stream of diborane at a pressure of 2 atm, passing at the rate of 70 cm³ per minute; the half-litre sample of diborane was cycled over the complex in this manner six times. Then it was possible to isolate 1·6 cm³ of $C_2H_5NHB_2H_5$, which was identified by its vapour tension of 19·5 mm at 0°. The accompanying H_2 amounted to 1·32 cm³.

The remaining complex seemed to have been little affected, again appearing as a translucent white solid. It was treated with 56·0 cm³ of HCl in ether at −78°, producing 23·67 cm³ of H_2, and then with water to complete the hydrolysis at room temperature. The total H_2 now was 79·8 cm³; expected for intact $C_2H_4NH \cdot BH_3$, 77·4 cm³. Since a part of the H_2 could have been due to the presence of a (—C—C—N—) polymerized $(C_2H_4NB_2H_5)_x$ in the solid, this result did not tell how much of the C_2N ring had resisted the diborane treatment; but a titration of the excess HCl showed that 46·25 cm³ (1·61 volumes) had been used. Now, since the amine would have neutralized 27·15 cm³ of HCl, the amount of HCl used for opening the ring must have been 19·1 cm³; i.e., no less than 66% of the C_2N rings had resisted opening prior to the HCl treatment.

Ethylaminodiborane from ethylamine and diborane—In lieu of a complete analysis of the aminodiborane obtained from C_2H_4NH and B_2H_6 (for it would have been very difficult to distinguish between $C_2H_5NHB_2H_5$ and the hypothetical $C_2H_4NB_2H_5$), ethylaminodiborane was prepared from ethylamine and diborane, for comparison. The method was the same as described earlier for methylaminodiborane: passage of diborane across $C_2H_5NH_2 \cdot BH_3$ at temperatures near 100°. After very careful purification, the sample melted at −96·2° (ethylenimine product, −96·4°), and it showed vapour tensions of 19·29 mm at 0·00° and 58·74 mm at 20·58° (calcd. from equation, 19·32 and 58·81). The close agreement left no doubt that the ethylenimine product also was ethylaminodiborane.

It is interesting that the volatility of ethylaminodiborane is appropriately less than that of its homologue methylaminodiborane, but very far less than that of its isomer dimethylaminodiborane. The explanation in terms of dipole shielding effects[1] continues to be applicable.

Acknowledgement—The generous support of this work by the Office of Naval Research is gratefully acknowledged. Reproduction in whole or in part is permitted for any purpose of the United States Government.

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J. Inorg. Nucl. Chem., 1956, Vol. 2, pp. 246 to 253. Pergamon Press Ltd., London

π-CYCLOPENTADIENYL COMPOUNDS OF URANIUM-IV AND THORIUM-IV

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(*Received* 27 *December* 1955)

Abstract—Uranium tetrachloride is allowed to react with sodium cyclopentadienide in tetrahydrofuran solution. On heating the dried product at 245° in vacuum, dark-red crystals of $(\pi\text{-}C_5H_5)_3UCl$ are obtained. Some chemical and physical properties of the compound are described. A molecular orbital view of the metal-to-ring bonding by W. MOFFITT is given. Evidence for the existence of π-cyclopentadienyl derivatives of thorium is presented.

1. URANIUM

THE characterization of cyclopentadienides of rare-earth elements[1] suggested the possibility that the heaviest elements in the lower-oxidation states might form similar ionic compounds.

The reaction of anhydrous uranium trichloride with sodium cyclopentadienide in tetrahydrofuran solution, followed by heating of the dried reaction mixture in vacuum, did indeed produce a red sublimate in yields of the order of a few per cent. This product was exceedingly reactive towards air and was thermally unstable, so that considerable decomposition occurred when attempts to resublime it were made. Analyses showed that the product was free from chloride, and that the composition was approximately $(C_5H_5)_3U$. In view of the low yields and of the difficulties of working with this substance, no further work was done. In some cases the product analysed $(C_5H_5)_2UCl$.

A similar reaction using anhydrous uranium tetrachloride with an excess of sodium cyclopentadienide gave a similar product. However, the reaction of uranium tetrachloride with sodium cyclopentadienide in the mole ratio 1 : 2·8 has allowed the isolation in almost quantitative yields, of a dark-red crystalline compound of the formula $C_{15}H_{15}UCl$.

No identifiable product has been obtained from the reaction of anhydrous uranyl chloride, UO_2Cl_2, with varying amounts of sodium cyclopentadienide, either by direct sublimation or by treatment of the reaction mixture with aqueous acid.

The nature of the bonds between the cyclopentadienyl rings and the uranium atom in $C_{15}H_{15}UCl$ is of interest. Unlike the cyclopentadienides of the rare earth[1] and other elements,[2] the uranium compound does not react with ferrous chloride in tetrahydrofuran; the formation of ferrocene by the reaction of cyclopentadienyl compounds with ferrous chloride was developed[1, 2] as a sensitive test for ionic dissociation leading to the cyclopentadienide ion $C_5H_5^-$. The failure of the uranium compound to react implies that the metal-to-ring bonds are not electrostatic in nature. Further, unlike the metal cyclopentadienides and the σ-cyclopentadienyl compounds,[3] there is no detectable reaction between $C_{15}H_{15}UCl$ and maleic

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[1] J. M. BIRMINGHAM and G. WILKINSON, *J. Amer. Chem. Soc.* **76**, 6210 (1954), and **78**, 422 (1956)

[3] G. WILKINSON, F. A. COTTON, and J. M. BIRMINGHAM, *J. Inorg. Nucl. Chem.* **2**, 95 (1956)

[2] Cf. T. S. PIPER and G. WILKINSON, *J. Inorg. Nucl. Chem.* **2**, 32 (1956).

anhydride; this failure to react is also in accordance with the view that the C_5H_5 rings are bound to the metal atom by a "sandwich-type" bond.

In tetrahydrofuran solutions, the compound shows only feeble electrical conductivity, but there is an instantaneous reaction with silver perchlorate in the solvent to give silver chloride; the chlorine in the compound thus appears to be ionically bound.

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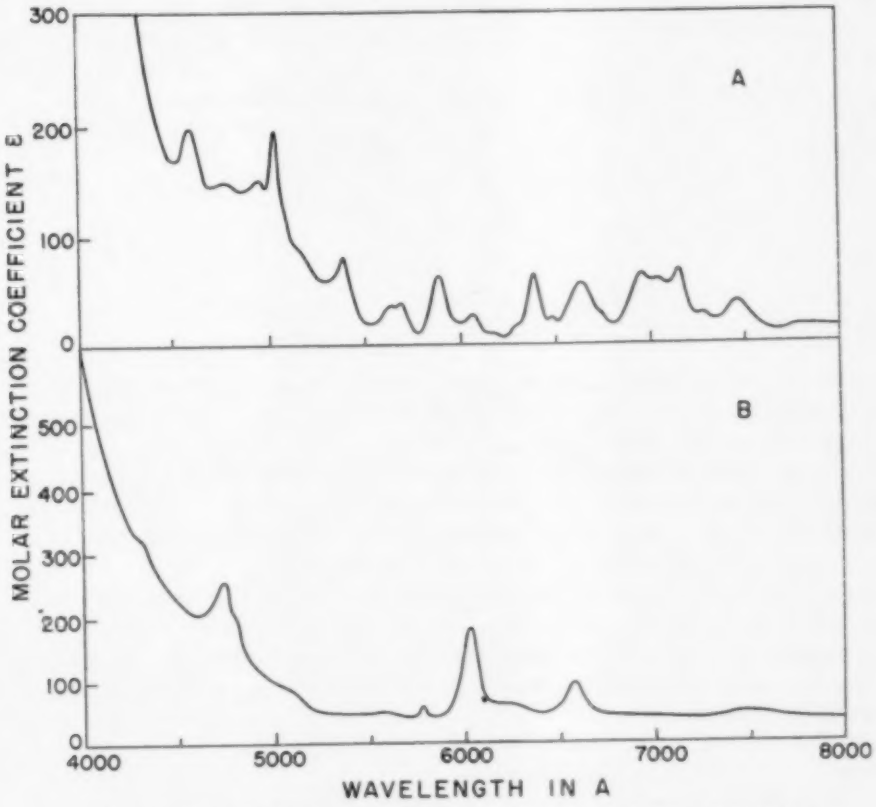

FIG. 1.—Absorption spectra of $(\pi\text{-}C_5H_5)_3UCl$. (a) in tetrahydrofuran (3·7 mM), (b) in water (2·0 mM). Cary Recording Spectrophotometer with 1-cm quartz cells.

In water, the compound is sparingly soluble to give a green solution. This solution is not very stable and begins to decompose after fifteen minutes or so. However, as with solutions of many other π-cyclopentadienyl metal cations, e.g. $[(\pi\text{-}C_5H_5)_2Fe]^+$, precipitates are formed with silicotungstic acid, and Reinecke's salt. It seems clear, therefore, that the cation $[(C_{15}H_{15})U]^+$ exists in aqueous solutions, probably as an aquated entity.

Other physical properties of $C_{15}H_{15}UCl$ are consistent with its formulation as a "sandwich-bonded" π-cyclopentadienyl compound, tri-(π-cyclopentadienyl)-uranium(IV) chloride, $(\pi\text{-}C_5H_5)_3UCl$. Thus the volatility is greater and the melting-point is considerably lower than is the case for the rare-earth cyclopentadienides of crystal radii for the metal ion comparable to the radius of uranium(IV). The absorption spectrum of $(\pi\text{-}C_5H_5)_3UCl$ in the visible region in tetrahydrofuran or pyridine

(Fig. 1) bears no resemblance to that of uranium(IV) in aqueous solution,[4] whereas the spectra of the rare-earth cyclopentadienides in tetrahydrofuran show considerable similarity to the spectra of the aquo ions. For $(\pi\text{-}C_5H_5)_3UCl$, not only are there many more sharp lines in the region 400–800 mμ, but also the molar extinction coefficients of the bands are generally much greater, e.g. at 715 mμ, $\varepsilon = 75$; at 502 mμ, $\varepsilon = 216$; at 458 mμ, $\varepsilon = 219$, than is the case with aquo uranium(IV) ions, where there are only four groups of bands in this region, all with molar extinction coefficients between 15 and 60. For aqueous solutions of $(\pi\text{-}C_5H_5)_3UCl$ (Fig. 1) there is some correspondence with the spectrum in tetrahydrofuran, but fewer bands are observed.

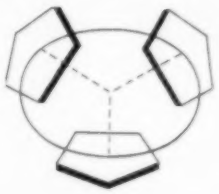

FIG. 2.

The only reasonable explanation for the chemical behaviour of $(\pi\text{-}C_5H_5)_3UCl$ and its aqueous solutions is that the three C_5H_5 rings are bound to the metal atom by "sandwich-type" homopolar bonds. For the π-cyclopentadienyl compounds of the transitional elements, where there are but two C_5H_5 rings bonded to the metal with known symmetry, the molecular orbital treatments[5, 6] have provided a satisfactory explanation of the bonding and of the chemical and magnetic properties of the compounds. It is of some interest, therefore, to investigate the conditions for similar bonding in the present case. The arrangement of the three rings around the metal atom is not known at the present time. For the rare-earth compounds $(C_5H_5)_3M$, it was suggested on electrostatic grounds that the cyclopentadienide ions would arrange themselves so that the axes through the centre of the rings and perpendicular to them, passing through the centre of the metal ion, would be coplanar and at angles of 120° to each other. We make the same assumption for the $[(\pi\text{-}C_5H_5)_3U]^+$ ion (cf. Fig. 2) although the bonds in this case are not ionic.

The following treatment is due to Professor W. MOFFITT of this Department.

The low-lying orbitals of the central uranium ion, outside the radon shell, are 5*f*, 6*d*, and 7*s*. These must be classified according to their behaviour under the symmetry elements of the assumed model (D_{3h})* for the ion $[(\pi\text{-}C_5H_5)_3U]^+$. Most importantly, there is the threefold axis C_3. When the orbitals remain invariant under this operation, they are called a; when they may be chosen so as to acquire factors $\exp(\pm 2\pi i/3)$, they are called $e_\pm$ and are doubly degenerate. Those orbitals which remain invariant under reflection in the horizontal plane of symmetry σ_h (perpendicular to the threefold axis), their representative symbols are primed $'$, whereas if they reverse their signs, these are doubly primed $''$. Finally, the nondegenerate a orbitals may be distinguished according to their behaviour under a rotation C_2 about

* It is most unlikely that there will be anything but weak orientational effects due to rotations of the cyclopentadienyl rings about their fivefold axes; these are therefore treated as circular disks so far as their interaction with the central ion is concerned.

[4] Cf. CHR. KLIXBULL-JØRGENSEN, *Kgl. Danske Vid. Selskab Mat.-fys. Medd.* **29**, (7) (1955).

[5] W. MOFFITT, *J. Amer. Chem. Soc.* **76**, 3386 (1954).

[6] J. D. DUNITZ and L. E. ORGEL, *J. Chem. Phys.* **23**, 954 (1955).

one of the twofold axes containing the nucleus of the central ion and the centroid of a cyclopentadienyl ring. If they are unchanged, we call them a_1; if they change sign, they are a_2. As a result, it is easily shown that the seven $5f$ orbitals are fa_1', fa_2', fa_2'', $fe_\pm'$, $fe_\pm''$, whereas the $6d$ and $7s$ orbitals are da_1', $de_\pm'$, $de_\pm''$, sa_1'. It remains to classify the orbitals of the cyclopentadienyl rings in the same basis.

The unsaturation electrons of a particular ring were called ψ_0, $\psi_{\pm 1}$, and $\psi_{\pm 2}$ in a previous paper.[5] Of these, the most stable ψ_0 orbital is assumed to be completely filled, and will concern us no more. In the ground and lower excited states, the antibonding $\psi_{\pm 2}$ orbitals are supposed to remain empty, and will also be ignored. We are therefore reduced to considering the doubly-degenerate $\psi_{\pm 1}$ pairs from each of the three rings, A, B, and C. Rather than using the complex forms $\psi_{\pm 1}$, themselves, it is more convenient to use their real and imaginary parts, which we may call ψ_A', ψ_A'' for ring A, say. As the notation implies, the former remains invariant and the latter changes sign under reflection in the plane σ_h. These may be combined to allow for the full molecular symmetry in the following manner:

$$cpa_2' = \frac{1}{\sqrt{3}}(\psi_A' + \psi_B' + \psi_C'),$$

$$cpa_2'' = \frac{1}{\sqrt{3}}(\psi_A'' + \psi_B'' + \psi_C''),$$

$$cpe_\pm' = \frac{1}{\sqrt{3}}(\psi_A' + \omega^{\pm 1}\psi_B' + \omega^{\pm 2}\psi_C'),$$

$$cpe_\pm'' = \frac{1}{\sqrt{3}}(\psi_A'' + \omega^{\pm 1}\psi_B'' + \omega^{\pm 2}\psi_C''),$$

where $\omega = \exp(2\pi i/3)$. There are five unsaturation electrons per cyclopentadienyl radical, regarded as a neutral species. Of these, two are assigned to the ψ_0 orbital. Accordingly, the valence shell of $\psi_\pm$ orbitals, which have been formed above, contains three holes: it can accommodate twelve electrons in all, but only nine are available from the radicals themselves. At any particular time, therefore, three electrons are in singly-occupied orbitals, and may form electron-pair bonds with electrons in orbitals of appropriate symmetry on the central ion.

From this point of view, the charge on the uranium atom is only $+1$, and it therefore has five electrons outside the radon shell. We see that the only possibilities for bonding in the a_2' and a_2'' orbital species are between the $5f$ electrons and the rings:

$$ba_2' = l_1 cpa_2' + m_1 fa_2',$$

$$ba_2'' = l_2 cpa_2'' + m_2 fa_2''$$

However, for bonding of $e_\pm'$ and $e_\pm''$ species, the ring orbitals may formally combine both with $6d$ and with $5f$ electrons. It is best, therefore, to construct from the latter pairs suitable hybrid orbitals:

$$je_\pm' = \cos\xi fe_\pm' + \sin\xi\, de_\pm',$$

$$je_\pm'' = \cos\eta fe_\pm'' + \sin\eta\, de_\pm'',$$

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for which the parameters ξ, η are chosen so as to give maximum overlap with the orbitals cpe', $cpe_{\pm}''$ respectively. The remaining hybrids

$$he_{\pm}' = \cos\xi\, de_{\pm}' - \sin\xi fe_{\pm}',$$

$$he_{\pm}'' = \cos\eta\, de_{\pm}'' - \sin\eta fe_{\pm}'',$$

are probably best regarded as nonbonding. The appropriate bonding molecular orbitals are therefore

$$be_{\pm}' = l_3 cpe_{\pm}' + m_3 je_{\pm}',$$

$$be_{\pm}'' = l_4 cpe_{\pm}'' + m_4 je_{\pm}''.$$

If, as seems reasonable, it were to be supposed that each of the bonding orbitals contains three times as many electrons from the cyclopentadienyl radicals as from the central ion,

$$|l_i|^2 \sim 3|m_i|^2, \qquad (i = 1, 2, 3, 4)$$

In this way, the rings would be described at electrically neutral. This will not be exactly true, of course, but it will give a reasonable approximation to the charge distribution, since the resulting single positive charge on the uranium atom may be efficiently solvated at the free positions on the C_3 axis, above and below the plane σ_h. On the average, therefore, three electrons from the central ion are used in binding the rings covalently, in which the $5f$ electrons play an important role.

The remaining two electrons on the uranium ion may be assigned in several different ways, the available orbitals being $he_{\pm}'$, $he_{\pm}''$, sa_1', da_1', and fa_1'. The last three will in general combine under the fields to which the ion is subject. Important contributions to these fields will be made by the solvating species or chloride ions, as well as the cyclopentadienyl rings. Paramagnetic resonance studies would assist greatly in making these assignments, but there are obvious difficulties in preparing suitable samples that consist of magnetically dilute single crystals, since no diamagnetic compound isomorphous with $(\pi\text{-}C_5H_5)_3UCl$ has yet been made. The susceptibility measurements show that two of these orbitals are singly occupied, and this is to be expected on most reasonable coupling schemes.

It should be remarked that our description allows for a continuous variation in the degree of ionicity of the bonds linking the rings to the ion. By allowing the $|l_i|$ to increase at the expense of the $|m_i|$, a maximum of one single negative charge may be acquired by each ring. It is hardly surprising, therefore, that the analogous compound of thorium—an element which achieves a rare-gas configuration in the IV oxidation state and is generally more electropositive on this account—should show such different chemical behaviour.

To summarize, those electrons of the complex $[(\pi\text{-}C_5H_5)U]^+$ ion—outside the radon shell of the central ion and the σ-electrons of the hydrocarbon rings—are assigned as follows:

$$(\psi_{0A})^2 \quad (\psi_{0B})^2 \quad (\psi_{0C})^2 \quad (ba_2')^2 \quad (ba_2'')^2 \quad (be')^4 \quad (be'')^4 \quad (n) \quad (\bar{n});$$

n, $\bar{n}$ are nonbonding orbitals on the uranium which it seems premature to identify more closely.

2. THORIUM

Attempts to prepare cyclopentadienyl derivatives of thorium have been only partially successful. From the dried reaction mixture of anhydrous thorium tetrachloride with an excess of sodium cyclopentadienide, a white sublimate, in yields of the order of 1 per cent, can be obtained by heating the mixture in vacuum at 250°C. This product is exceedingly reactive with air and also decomposes thermally on sublimation, so that purification is impossible. Analyses of the product for thorium indicate the approximate composition $(C_5H_5)_4Th$. The substance resembles the rare-earth cyclopentadienides. On allowing thorium tetrachloride to react for several hours with sodium cyclopentadienide in the mole ratio 1 : 2 in tetrahydrofuran solution, and subsequently extracting the evaporated mixture with 6 N hydrochloric acid, a colourless solution is obtained. This solution decomposes rapidly, so that although it has been shown to give precipitation reactions characteristic of di-(π-cyclopentadienyl) metal cations, e.g. with silicotungstic acid, Reinecke's salt, and bromine water, pure compounds cannot be obtained in this way. Infra-red spectra of the dried precipitates in potassium halide windows are similar to those of the di-(π-cyclopentadienyl) zirconium[7] compounds. Attempts to obtain the simple thorium chloride and iodide compounds by extraction with and crystallization from polar solvents have failed.

The precipitation reactions of the aqueous solutions suggest that thorium does form di-(π-cyclopentadienyl) metal halides similar to those of titanium and zirconium, but that the thorium compounds are more ionic and also undergo hydrolytic decomposition much more readily, even in strong acid solution, than do their titanium and zirconium analogues. The possibility that the thorium cation is the $[(\pi\text{-}C_5H_5)_3Th]^+$ ion is, of course, not eliminated, but the usual similarity of zirconium, hafnium, and thorium leads us to favour the ion with only two rings per metal atom.

3. EXPERIMENTAL

Uranium tetrachloride was prepared by the direct action of pure chlorine on uranium metal (Fisher Scientific Co., technical grade, fused rods) at 650°C. Thorium tetrachloride was made by passing carbon tetrachloride vapour over thorium oxide at 800°C for several hours.

Tetrahydrofuran was purified by distillation in nitrogen over lithium aluminium hydride; for special purposes the solvent was distilled in a vacuum system.

All preparations and operations were performed under nitrogen or in vacuum.

Preparation of tri(π-cyclopentadienyl)uranium(IV) chloride, $(\pi\text{-}C_5H_5)_3UCl$

A solution of sodium cyclopentadienide (0·18 mol) in tetrahydrofuran (250 ml) was added very slowly with cooling to a solution of uranium tetrachloride (0·063 mol) in tetrahydrofuran (250 ml). This mixture was stirred rapidly for a few hours under reflux. The solvent was removed and the residue transferred to a sublimation vessel. At 245°C at 10^{-4} to 10^{-5} mm Hg, dark-red, almost black crystals collected on a water-cooled probe. The compound was purified by resublimation. Yield, 19–19·5 g (82–85% based on UCl_4).

Analysis[8]—Required for $(\pi\text{-}C_5H_5)_3UCl$: C 38·5, H 3·4, Cl 7·55, U 50·8; found: C 37·7, H 3·1, Cl 7·63, U 50·6.

Properties of $(\pi\text{-}C_5H_5)_3UCl$

The compound is exceedingly reactive towards air, and all operations with it were carried out either in vacuum or in an inert atmosphere. Chemical reactions were carried out using break-seal tubes, and all solvents or reagents were deaerated on a vacuum system. The compound is thermally

[7] G. WILKINSON and J. M. BIRMINGHAM, *J. Amer. Chem. Soc.* 76, 4281 (1954).

[8] We are indebted to Dr. E. O. BRIMM, Linde Air Products Co., Tonawanda, New York, for arranging for carbon and hydrogen analyses of this compound.

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stable to at least 300°C, and in an evacuated sealed tube melts to a red liquid at 260–265°C; it can be sublimed in vacuum at temperatures above 180°C. The compound is completely and instantly destroyed on exposure to air. It is insoluble in petroleum ether and in benzene, but is readily soluble in tetrahydrofuran and pyridine, giving deep red-brown solutions. These solutions, which are exceedingly sensitive to traces of oxygen, slowly decompose on standing, so that attempts to measure the molecular weight of the compound by the method of isothermal distillation were unsuccessful. The compound is almost insoluble in carbon tetrachloride, but has a rather low solubility in carbon disulphide, chloroform, and dichloromethane; some decomposition occurs in these solvents on standing.

On treating solutions of the compound in tetrahydrofuran with ferrous chloride, prepared in tetrahydrofuran by reduction of ferric chloride with iron powder,[2] there is no reaction at room temperature. When the mixture was kept at 100°C for eight days, some decomposition of the solution occurred, and a trace of ferrocene (~1 mg) was detected from ~500 mg (π-$C_5H_5)_3UCl$ after evaporation of the ether and extraction with petroleum ether.

In tetrahydrofuran, there is no apparent reaction between (π-$C_5H_5)_3UCl$ and maleic anhydride in the cold or on warming. With silver perchlorate in the same solvent, (π-$C_5H_5)_3UCl$ gives an immediate precipitate of silver chloride, and the residual red-brown solution soon undergoes extensive decomposition. On addition of small amounts of water, the tetrahydrofuran solutions of (π-$C_5H_5)_3UCl$ turn green (see below).

Aqueous solutions of (π-$C_5H_5)_3UCl$

The compound is not wetted by water, but on grinding the solid with thoroughly deaerated water in a nitrogen-filled gloved box, a green solution is obtained. This solution is exceedingly readily oxidized by air and also decomposes slowly on standing. The solution gives precipitates with silicotungstic acid, chloroplatinic acid, Reinecke's salt, and potassium tri-iodide. The chloroplatinate forms olive-green needle crystals. The (π-$C_5H_5)_3UCl$ is very sparingly soluble in 12 N hydrochloric acid, giving amethyst-coloured solutions similar to those of the tetrahydrofuran solutions. The suppression of the dissociation of chlorine in the green aqueous solutions on addition of hydrochloric acid is also shown by a change in colour towards the red.

Analyses of the Reineckate, which had been dried in vacuum for several hours, were made. Required for [(π-$C_5H_5)_3U$] [$Cr(NH_3)_2(SCN)_4$]$3H_2O$: U 29·6, Cr 6·45; found: U 29·5, Cr 6·34.

Magnetic measurements

The magnetic susceptibility of (π-$C_5H_5)_3UCl$ has been measured in the solid phase and also in solution in tetrahydrofuran, using methods described previously.[2] For the finely ground solid, the measured molar susceptibility values, corrected for diamagnetism (-160×10^{-6} c.g.s.u.) of the C_5H_5 rings and chlorine, are: 77°K, 6280×10^{-6}; 195°K, 4300×10^{-6}; 273°K, 3440×10^{-6}; 306°K, 3220×10^{-6} c.g.s.u. The compound thus follows the Curie-Weiss law, $\mu = 2{\cdot}04\sqrt{(T + \Delta)\chi_{mol}}$ with $\Delta = 138°$ and $\mu = 3{\cdot}16$ B.M. In tetrahydrofuran solution (0·240 M) the corrected molar susceptibility was $\chi_{mol}^{305°} = 2890 \times 10^{-6}$ c.g.s.u.; using the spin only formula, $\mu_{eff} = 2{\cdot}72$ B.M. The susceptibility values are good to about 3%. It seems reasonable to conclude that in (π-$C_5H_5)_3UCl$ there are two unpaired electrons, but this fact provides no evidence regarding the nature of the metal-to-ring bonds.

Conductivity measurements

Conductivity measurements were made, using a closed cell with grey platinum electrodes, which could be attached to a vacuum system for admission of (π-$C_5H_5)_3UCl$ and the tetrahydrofuran solvent. The cell was calibrated, using potassium chloride solutions. An A. H. Thomas Serfass conductivity bridge was used.

The compound forms very weakly conducting solutions; at 0·025 M, $\Lambda = 3{\cdot}6 \times 10^{-2}$; at 0·0135 M, $\Lambda = 5{\cdot}3 \times 10^{-2}$; at 0·009 M, $\Lambda = 6{\cdot}5 \times 10^{-2}$ ohms^{-1} cm^3 g eq.$^{-1}$

Analyses

After destruction of organic matter, the uranium solutions were reduced in a Jones reductor and were then oxidized by air to uranium(IV). An excess of ferric sulphate solution was added and the ferrous ion formed was then titrated potentiometrically with standard ceric sulphate solution.

The small quantities of uranium involved in spectral measurements, etc., were determined spectrophotometrically.[9]

Chromium was determined by addition of ferrous ion to the persulphate oxidized solution and titration of the excess potentiometrically with ceric sulphate.

Chloride was determined gravimetrically.

Spectra

The solutions were made up in cells which were attached to a vacuum line; after running in the solutions, the cells were sealed off. The uranium content of the solutions was determined subsequently by analysis. A Cary recording spectrophotometer was used.

The spectra in pyridine were identical with those in tetrahydrofuran.

Infra-red spectra were taken on a Model 21 Perkin-Elmer double-beam recording spectrophotometer. In carbon disulphide the solubility of $(\pi\text{-}C_5H_5)_3UCl$ is so low that only the strong bands at 1010 and 784 cm^{-1}, which fall in the region where other π-cyclopentadienyl compounds show strong absorptions, were well defined. When the spectra were taken within ten minutes of the preparation of the solution in a gloved box, two weak bands in the C-H stretching region at 2922 and 3096 cm^{-1} were observed. The former is attributable to decomposition of $(\pi\text{-}C_5H_5)_3UCl$ in carbon disulphide since, when the specimen is left standing, this band increases in intensity at the expense of the 3096-cm^{-1} band. The latter is in the region of the C-H stretching frequencies in other π-cyclopentadienyl compounds. The bands at 1010 and 784 cm^{-1} also decrease in intensity with time, again indicating reaction of the compound with the solvent.

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Acknowledgements—We are indebted to the National Science Foundation for a predoctoral fellowship (L. T. R.) and to the Mallinckrodt Chemical Co. for partial support of laboratory expenses.

This work was also supported in part by the Atomic Energy Commision.

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THE SYSTEMS FORMED BY ZIRCONIUM AND HAFNIUM TETRACHLORIDE WITH ACETONITRILE AND ISOAMYL ETHER*

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(*Received* 19 *August* 1955)

Abstract—The system zirconium (hafnium) tetrachloride, isoamyl ether, and acetonitrile shows a binodal curve which is truncated by a line representing equilibrium of a solid phase, $MCl_4 : 2CH_3CN$ with two liquid phases of varying compositions. The compound MCl_4 : 2 isoamyl ether was observed only in equilibrium with a saturated solution of the pure solvent. Only a slight difference in the distribution of zirconium and hafnium between the two phases was noted. The solutes concentrated in the acetonitrile phase, and the hafnium did so to a slightly greater extent than did the zirconium. The maximum separation factor was Hf/Zr = 1·8.

INTRODUCTION

THE distribution of transition element compounds between two immiscible organic solvents is a little-studied field. A search of the literature dealing with liquid ternary and quaternary systems, in general, has been made by SMITH.[1] Conspicuously absent from this were solutes which were compounds of the transition metals. Some work has been reported recently on systems of the type transition metal salt-organic solvent-water.[2, 3, 4, 5, 6] However, none with another organic liquid as the second solvent have been studied.

In addition, the solutes being considered, zirconium and hafnium tetrachlorides are extensively hydrolysed and polymerized in aqueous solution, thus complicating distribution systems designed for the extraction of these elements. It was thought that a completely nonaqueous system would have an advantage over aqueous systems in this respect. To make this study, the following experimental conditions had to be met.

(a) Pairs of liquids were desired which were partially miscible, and yet which dissolved an appreciable amount of the metal tetrachloride.

(b) Only solvents which did not react extensively with the metal tetrachlorides were sought. Solvents which reacted to yield hydrogen chloride, or which underwent extensive organic reactions as evidenced by colour development, were eliminated. Thus unsaturated and hydroxylated organic compounds were not considered.

(c) The ease with which the tetrahalides hydrolyse required the development of a technique for equilibration and sampling of the system in the absence of the atmosphere.

* Based on a thesis submitted by LAVERNE E. TREVORROW in partial fulfilment of the requirements for the degree of Doctor of Philosophy, and supported in part by the Office of Naval Research.

[1] J. C. SMITH, *Industr. Eng. Chem.* **41**, 2932–37 (1949); *ibid.*, 1438 (1950).
[2] L. I. KATZIN and J. R. FERRARO, *J. Amer. Chem. Soc.* **72**, 5461–1 (1950); **74**, 2572–4 (1952); **75**, 3825–7 (1953).
[3] C. C. TEMPLETON and L. K. DALY, *ibid.* **73**, 3989–91 (1951).
[4] C. C. TEMPLETON, *J. Phys. Colloid. Chem.* **54**, 1255-69 (1950).
[5] L. I. KATZIN and J. C. SULLIVAN, *ibid.* **55**, 346–74 (1951).
[6] C. C. TEMPLETON and L. K. DALY, *J. Phys. Chem.* **56**, 215–17 (1952).

The metal tetrahalides are Lewis acids, and it was therefore supposed that some of the Lewis bases would be good solvents for them. With the above restrictions and ideas in mind, a strictly empirical approach was used to find a suitable solvent pair. From a large number of qualitative observations on solvent miscibilities, and on the interaction of zirconium tetrachloride with various solvents, acetonitrile and isoamyl ether were chosen for this work.

EXPERIMENTAL

Materials—The zirconium dioxide and hafnium dioxide used as source materials contained only 58 p.p.m. of hafnium and 1% zirconium respectively. A second source of hafnium oxide contained about 2% zirconium. Atomic weights were corrected accordingly.

Zirconium and hafnium tetrahalides were prepared by mixing the corresponding dioxides with charcoal and passing chlorine gas over the mixture at 600°. The crude tetrachloride was purified by first subliming in an atmosphere of hydrogen and then resubliming several times *in vacuo*, and finally condensing into small ampules, which were then sealed off and stored.

The acetonitrile and isoamyl ether were distilled off dehydrating agents in an all-glass apparatus into receiving flasks suitably protected from the atmosphere. The drying agent for acetonitrile was phosphorus pentoxide. The ether was treated to remove the peroxides present, initially dried over calcium chloride, and finally over sodium ribbon. The purity of the product in each case was checked by measuring its index of refraction. The acetonitrile had an index of refraction $n_D^{25°} = 1{\cdot}3418 \pm 0{\cdot}0002$ compared to the literature value[7] corrected to 25° of $n_D = 1{\cdot}3421 \pm 0{\cdot}0002$. For isoamyl ether our product had an index of refraction, $n_D^{25°} = 1{\cdot}4059 \pm 0{\cdot}0001$, compared to the average literature value[8] for the ether, from two different sources corrected to 25°, of $n_D = 1{\cdot}4062 \pm 0{\cdot}0005$.

Analytical methods—In the analysis of zirconium and hafnium compounds contained in the organic phases, the solution was added to an excess of water, and the resulting mixture was boiled vigorously until the solvents had been steam-distilled out. The zirconium or hafnium was then precipitated as the hydrated oxide with freshly prepared aqueous ammonia.

The analysis of solid zirconium or hafnium compounds with organic components was carried out as follows: (1) Solids to be analysed for nitrogen were dissolved in and made up to volume in a volumetric flask, with glacial acetic acid. Aliquots were then taken for Kjeldahl nitrogen analysis,[9] as well as metal analysis by the above procedure. (2) Solids which did not require nitrogen analysis were hydrolysed in water, the organic solvent steam-distilled out, and the hydrated oxide precipitated. No analyses were made for the ether. Its percentage was obtained by difference.

Procedure—The temperature chosen for this study was 25°, which is just below the critical solution temperature of 27·9°. At 25° two liquid phases appeared at 28 and 62 weight per cent acetonitrile (Fig. 2, *G*, *H*).

The three-component mixtures were prepared by sublimation *in vacuo* of metal tetrachloride from one of the stock ampules into a cell. After the stock ampule had been sealed off from the vacuum manifold, the cell containing metal tetrachloride was brought to atmospheric pressure by the admission of dry air. The cell was then quickly transferred to a paraffin-oil-sealed stirrer assembly, and then thermostatted, as shown in Fig. 1. Although the organic solvents were originally added to the cell by means of weight burets attached to the cell by ground-glass joints, in the final version of the cell the joints were replaced by serum-bottle caps, and the weight burets by hypodermic syringes. This provided a neater method of introducing the solvents without exposure to the atmosphere. By alternately titrating with one solvent and then the other, a series of clear and cloud points were obtained which outlined the acetonitrile-rich side of the binodal curve (Fig. 2, *B*, *H*).

The points on the isoamyl ether-rich side of the binodal curve (Fig. 2, *A*, *G*) were obtained by starting with a homogeneous, ether-rich solvent mixture in the cell, and titrating with a solution of metal tetrachloride in acetonitrile until the two-liquid-phase region was reached.

The exact locations of points *A* and *B* were determined by the interaction of the solubility line with the liquid-liquid curves.

[7] G. H. Jeffery and A. I. Vogel, *J. Chem. Soc.* 674 (1948).
[8] A. I. Vogel, *J. Chem. Soc.* 616 (1948).
[9] H. Vanetten and M. B. Wiele, *Anal. Chem.* **23**, 1338–9 (1951).

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The points on the line representing equilibrium between the solid phase and the mixed solvent were determined by adding various solvent mixtures to metal tetrachloride with stirring until the last particle of solid phase just disappeared. Those solvent mixtures which existed as two phases at room temperature were warmed from a distance with an infra-red lamp, so that a homogeneous mixture was delivered into the cell. These titrations were performed slowly, and it was assumed that the droplets being titrated into the cell quickly attained the temperature of the thermostat. Thus there was probably no appreciable error due to the dissolution of the solid in a solvent at a temperature above that of the thermostat.

For the preparation of samples from which the solid phases could be recovered, cells containing a sintered glass disk of medium porosity were used. Metal tetrachloride was sublimed into the cell in the usual manner and, after the stock ampule had been sealed off, amounts of the two organic

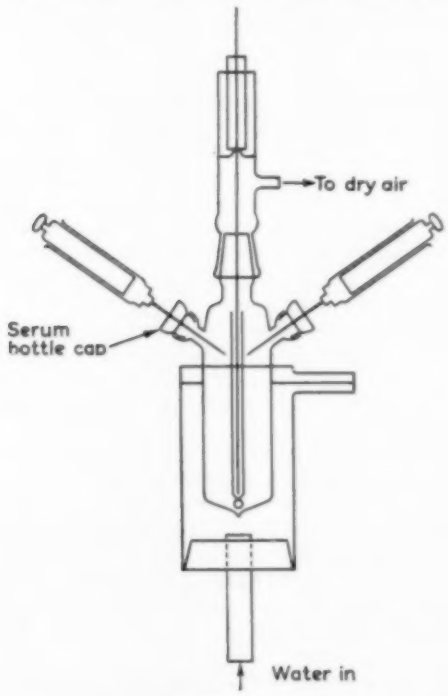

FIG. 1.

solvents were added by means of hypodermic syringes through a side arm bearing a serum-bottle cap. When the cell had been sealed, it was agitated in the constant-temperature bath for at least one week. After equilibration, the tips of the cell were cracked off, and the supernatant liquid forced through the glass frit under nitrogen pressure into a weighing bottle. The cell was closed with stoppers and weighed, then the solid was washed out, and the cell dried and weighed again. Such samples provided two things:

1. The composition of the solid phase in equilibrium with saturated solution was obtained by the method of wet residues.

2. The points representing compositions of the saturated solutions lie on the solubility line obtained by the titration method of determining the solubility of the solid phase. Therefore it was concluded that equilibrium had been reached in the titration experiments.

Distribution experiments were set up in the following manner. The three components were mixed in cells constructed of 25-mm tubing. The metal tetrachloride was sublimed in as usual, and then the organic components introduced via hypodermic syringes through a serum-bottle cap. About 17·5 ml of isoamyl ether and 7·5 ml of acetonitrile were used in the make-up of the samples. Thus,

isoamyl ether made up about 70% by volume of the total solvent. The cell was then cooled, sealed off from the vacuum manifold, and placed in the thermostat at 25°. These samples received end-over-end rotation in the thermostat overnight. After rotation, the tubes were allowed to stand upright for ten minutes or more to allow separation of the two phases. The two layers were sampled with hypodermic syringes, and analysed.

DISCUSSION

Owing to the similarity in the ternary systems of zirconium and hafnium tetrachlorides, only the complete zirconium diagram is given; the corresponding hafnium points are indicated by the primed letters. The data for the important points are given in Table 1.

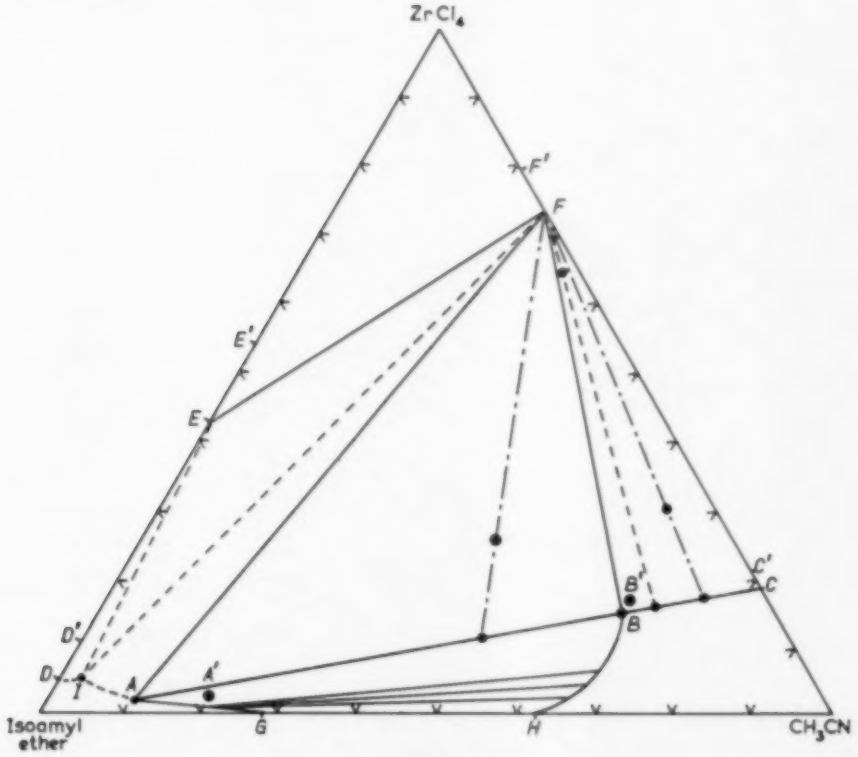

FIG. 2.

In a system of three liquid components, two of which are incompletely miscible, usually a smooth, umbrella-shaped binodal curve is obtained. However, this is a three-component system, containing two incompletely miscible liquids and a solid phase. In this case, the binodal curve is truncated by a line *BA* representing the solubility of the solid phase in liquid mixtures of varying composition. The solid phase existing in equilibrium with the solutions along the entire line *CBA* was $MCl_4 : 2CH_3CN$ (F), as shown by the method of wet residues (long and short dashed lines), as well as by the direct analysis of the solid recovered from pure acetonitrile. The material recovered from pure isoamyl ether approached the 1 : 2 ratio (*E*), but was always low in isoamyl ether content. The weight solubilities of the hafnium addition

compounds in acetonitrile (C') and isoamyl ether (D') were slightly greater than the solubilities of the corresponding zirconium compounds (C and D).

The acetonitrile addition compound coexists with an isoamyl ether-rich single homogeneous liquid phase beyond point A, although we were unable to elucidate this portion of the system owing to difficulties in observing the cloud and clear points

TABLE 1.

Point on Fig. 2	CH_3CN	Composition weight % MCl_4	Isoamyl ether
A	Zr 6 Hf 12	1·6 2·0	92·4 86
B	Zr 66 Hf 66	15 16	19 18
C	Zr 81·9 ± 0·8 Hf 79·6 ± 0·4	18·1 ± 0·8 20·4 ± 0·4	— —
D	Zr — Hf —	5·50 ± 0·9 10·5	94·5 ± 0·9 89·5
		Mole Ratio	
E	Zr — Hf —	1 1	1·78 ± 0·10 1·86 ± 0·10
F	Zr 1·96 ± 0·03 Hf 1·98 ± 0·02	1 1	— —

in mixtures involving very high isoamyl ether concentrations, and very low metal concentrations. Attempts to titrate a solution of composition D always yielded a precipitate upon addition of the first drop of acetonitrile. Some comments should be made concerning the nature region, however.

The acetonitrile addition compounds are much more stable than the isoamyl ether compounds, and the addition of a few drops of acetonitrile to a saturated solution of the isoamyl ether compound results in the formation of the acetonitrile addition compound. Since acetonitrile has a small molecular weight compared to the isoamyl ether, a few drops of acetonitrile contain sufficient moles to convert the isoamyl ether addition compound to the acetonitrile addition compound. At point A, the mol ratio of acetonitrile to metal tetrachloride is about 33 : 1. Since point A is an invarient point, the line CBA must continue past A. Beyond A the solid is in equilibrium with a single liquid phase and the system now has one degree of freedom.

As the acetonitrile content decreases further, a second solid phase of composition *E* must appear. This point is designated *I*, and the associated lines are dashed to indicate that their placement is speculatory. Beyond *I* there must exist a very shallow region of solid *E* in equilibrium with a single homogeneous phase.

It is interesting to note that the isoamyl ether content of the acetonitrile-rich phase and the acetonitrile content of the isoamyl ether-rich phase both decreased as the metal tetrachloride content increased along lines *GA* and *HB*.

Distribution measurements were made with ternary mixtures having total compositions within the *GABH* region of the three-component diagram. The distribution ratio *D* (Table 2) was calculated as the ratio of the molality of the metal tetrachloride of the acetonitrile-rich phase to the molality of the metal tetrachloride of the isoamyl ether-rich phase.

TABLE 2.—DISTRIBUTION DATA

	Molalities		Distribution ratio
	Ether	Nitrile	
Zr	0·0218	0·0998	4·58
	0·0303	0·192	6·34
	0·0330	0·280	8·48
	0·016	0·592	37·00
	0·019	2·74	144·2
Hf	0·0150	0·0902	6·01
	0·0195	0·192	9·85
	0·0186	0·187	10·05
	0·0197	0·322	16·35
	0·0175	0·478	27·31
	0·0172	0·510	29·65

The metal concentrates preferentially in the acetonitrile phase, with the hafnium doing so to a slightly greater extent than the zirconium. The maximum separation factor $D_{Hf/Zr}$ is about 1·8 in favour of the hafnium at 0·24 molal acetonitrile-rich phase.

These data are internally consistent with the phase diagram. Although for both the zirconium and hafnium system points *G* and *H* must be the same, the difference in the composition of the point *A* for zirconium and hafnium gives a slightly different slope to the line *GA* for each element, and although point *B* is very similar for the two elements, the bow in the line *BH* is slightly different for each. This results in a maximum in the separation factor. The tie lines given are for zirconium; those for hafnium have a greater slope. In comparing these data, one must keep in mind that the phase diagram is given in weight per cent, and that the distribution data are calculated on the basis of molalities.

It is concluded that this particular extraction system does not show a large enough separation factor for practical use. However, systems of this general type bear further investigation.

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J. Inorg. Nucl. Chem., 1956, Vol. 2, pp. 260 to 262. Pergamon Press Ltd., London

THE ISOTOPIC EXCHANGE OF ARSENIC TRICHLORIDE AND CHLORINE

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(*Received* 5 *December* 1955)

Abstract—We have measured the rate of exchange of isotopic chlorine between arsenic trichloride and chlorine in carbon tetrachloride solution. We find no simple mechanism indicated, the reaction is catalysed by hydrogen chloride, and the formation of arsenic pentachloride is shown to be very unlikely.

IN many of its compounds, arsenic shows a reluctance to assume a co-ordination number of 5, whereas other members of this family form such compounds readily. The use of 4*f* orbitals in bonding by members of the second long period[1] might explain the penta-co-ordination of antimony, but we cannot fully explain the anomalous position of arsenic with respect to phosphorus and antimony. Arsenic pentafluoride is known, but dissociates readily. Despite a claim,[2] the preparation of arsenic pentachloride as a stable compound has not been accomplished.

In connection with our work on isotopic exchange reactions of penta-co-ordinated species,[3] we have measured the rate of exchange of chlorine atoms between arsenic trichloride and chlorine in carbon tetrachloride solution. It is easy to see that a very favourable path for exchange would be via the formation of arsenic pentachloride; our results indicate such a compound does not exist.

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In general, the procedures and precautions against the intrusion of moisture were similar to those used previously.[3] All operations which might introduce moisture were done in an all-glass system using high-vacuum techniques, or in a dry-box atmosphere having a dew-point of less than $-60°$.

Arsenic trichloride, reagent grade, was further purified by triple-vacuum distillation, each time from room temperature to a trap cooled to $-80°$. Arsenic trichloride-Cl^{36} was prepared by the reaction of hydrogen chloride-Cl^{36}[4] and arsenic trichloride for 24 h at 100°. Equilibration was complete, and the arsenic trichloride was separated from hydrogen chloride by another set of vacuum distillations as above.

A run was made as follows. Solutions of the reactants in carbon tetrachloride were prepared inside the dry box and mixed by pouring into calibrated reaction tubes. After a preselected time, a reaction tube was emptied into a flask, the chlorine evaporated by a stream of nitrogen, and the chlorine-nitrogen mixture conducted to a cold trap outside the dry box. Preliminary experiments showed that separation was essentially complete in a 30-sec evaporation; no arsenic trichloride could be detected in the chlorine sample.

A single run was made with hydrogen chloride (in place of chlorine) exchanging with arsenic trichloride. Exchange was complete in less than 6 min, faster than we could conveniently measure.

* From the M.S. Thesis of J. H. O., Florida State University, 1955. Present address: Savannah River Plant, Aiken, South Carolina.

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[4] Received on allocation from the U.S. Atomic Energy Commission.

All runs were made at room temperature (24·5 ± 0·5°). Decreasing the level of illumination by wrapping the reaction tubes in aluminium foil or shielding the dry box with red cellophane had no effect on the speed of the reaction. A number of reaction tubes of different sizes were used without any apparent effect on the rate.

RESULTS AND DISCUSSION

Each experimental run showed a straight-line graph of log $(1 - F)$ vs. time, indicating that a homogeneous isotopic exchange reaction was occurring. Within experimental error, the line extrapolated back to zero exchange at zero time, which means that the separation procedure was not inducing exchange. For each run, the exchange rate-constant R was calculated by

$$R = \frac{3\,[AsCl_3]\,2\,[Cl_2]}{3\,[AsCl_3] + 2\,[Cl_2]} \cdot \frac{0{\cdot}693}{t_{\frac{1}{2}}} \qquad (1)$$

and the results are given in Table 1. It was apparent that hydrogen chloride had a powerful catalytic effect on the reaction rate; the A, B sets of runs represent an effort to offset the catalysis. In each A, B set, the reactants were prepared simultaneously

TABLE 1.

Run	Concentration g.f.w. Cl/l. × 10^3		$t_{\frac{1}{2}}$ (hours)	$R \times 10^3$
	Cl_2	$AsCl_3$		
1	5·40	2·40	2·5	4·6
2A	3·88	2·66	15·0	0·73
2B	3·88	5·33	2·5	6·2
3	3·00	19·2	8·9	2·0
4	8·16	12·0	7·3	4·6
5	10·4	21·3	<0·2	>240[a]
6	10·1	15·0	2·2	19·4
7A	7·36	11·3	5·6	5·5
7B	7·36	5·66	4·0	5·5
8A	7·48	12·5	0·65	50
8B	5·02	12·5	2·3	11·4
9A	7·40	12·1	6·7	4·7
9B	3·54	12·1	6·9	2·7
10	7·08	11·6	8·0	3·8
11A	11·1	16·6	3·8	12·1
11B	11·1	4·76	7·4	2·8
12	6·90	6·40	<0·02	>1200[b]
13	3·55	12·0	2·0	9·5

[a] A small (unknown) amount of HCl present in the chlorine. Exchange complete in less than one hour

[b] 0·020 g.f.w./l. of HCl added to the reaction mixture. Exchange complete in six minutes.

and from the same batches of arsenic trichloride, chlorine, and carbon tetrachloride. By comparing 7A,B and 11A,B, or comparing 8A,B and 9A,B, for example, it is seen that there is still a catalytic effect, due most probably to hydrogen chloride.

Because of the catalysis, the exact mechanism of exchange cannot be studied by our methods. In the presence of any reasonable added amount of hydrogen chloride,

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see Run 12, the rate is immeasurably fast. We suspect, in fact, that the mechanism of exchange *must* involve hydrogen chloride, and maybe there is no direct exchange of chlorine atoms between arsenic trichloride and chlorine. As mentioned above, we tested the exchange of arsenic trichloride and hydrogen chloride in carbon tetrachloride solution, and found it immeasurably fast, in accordance with the results of CLUSIUS and HAIMERL.[5] We certainly expect that the hydrogen chloride-chlorine exchange also would be rapid, in accord with the work of JOHNSTON and LIBBY.[6]

Two things, then, indicate against the direct formation of arsenic pentachloride by a combination reaction. The exchange reaction is not first-order in chlorine concentration and first order in arsenic trichloride concentration, as it should be to lead to arsenic pentachloride as a reaction intermediate. Secondly, the exchange is relatively slow. Since phosphorus trichloride and chlorine combine very rapidly, we might expect the arsenic reaction to be rapid also. This would lead to an exchange as rapid as the combination reaction, whereas the exchange reactions have half-lives of the order of hours. Similarly, the experimental data obviate a mechanism involving a first step as follows:

$$AsCl_3 \rightleftarrows AsCl_2 + {}^{\cdot}Cl \qquad (2)$$

as postulated[7] for the exchange of arsenic between arsenic trichloride and arsenic tribromide. Such a step as eq. (2) would lead to a first-order dependence on arsenic trichloride concentration.

We have considered a number of ways in which arsenic trichloride and hydrogen chloride may exchange chlorine atoms. Perhaps the most reasonable is the direct addition as follows:

$$HCl + AsCl_3 \rightleftarrows HAsCl_4 \qquad (3)$$

This compound is similar to the aryl tetrachloro arsenic compounds,[8] and we would expect an equilibration of activity. The hydrogen tetrachloro arsenic would be very unstable and perhaps only tetra-co-ordinated.

We are happy to acknowledge the assistance given by the Air Reduction Company, which donated the liquid nitrogen used in this work. This work was performed on Contract No. AT-(40-1)-1317 with the Atomic Energy Commission.

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Relative Yields of Californium Isotopes produced in the Bombardment of Uranium with Carbon-12 and Carbon-13 Ions

(*Received* 4 *January* 1956)

THE production of californium isotopes from uranium bombarded with heavy ions was reported by GHIORSO *et al.*[1] in 1951, the reactions being:

$$U^{238}(C^{12}, 4n)Cf^{246}\ (36\ h)$$

$$U^{238}(C^{12}, 5n)Cf^{245}\ (45\ min)$$

THE 45-min isotope was originally reported as Cf^{244}, but is now known to be Cf^{245}.[2] The extremely low yields obtained are believed to be due to the very high probability of prompt fission of the highly excited compound nucleus produced. In general, the products of such heavy-ion bombardments are very neutron-deficient, and therefore have short half-lives for α- and electron-capture decay. Every extra neutron in either target or projectile nucleus is likely to reduce these difficulties and, in order to assess the value of extra neutrons in the projectile, a comparison has been made between the yields of α-emitting californium isotopes produced by bombarding uranium with the two isotopes of carbon.

Uranium foils were bombarded with internal beams of carbon ions in the Birmingham University cyclotron. Owing to the complicated mechanism of acceleration,[3] the energies of the ions were not well defined; although the peak energy of ions of either kind was over 100 MeV, the mean was in the region of 65 MeV, well below the potential barrier of uranium. Beam currents of 0·01 to 0·04 μA of ions above 70 MeV were used, and each bombardment lasted about an hour.

After bombardment, the uranium foils were dissolved, and uranium was removed quantitatively by absorption on an anion exchange resin of the chloride complex in 7 N HCl solution. The californium fraction, free of other transuranium elements, was isolated by elution from a cation-exchange column with ammonium lactate.[4] The chemical processing was normally completed in 30–45 min after the end of bombardment.

The sources were placed in an α-particle gridded ionization chamber, the pulses from which were fed to a 100-channel pulse analyser. The 6·75-MeV peak due to α-particles from Cf^{246} (36 h) was completely resolved from the 7·15-MeV peak due to Cf^{245} (45 min).

The results of four bombardments with C^{12} ions and of five with C^{13} ions are shown in the table below. Except in the case where only one experiment was carried out, the yields are the mean of two or three experiments.

[1] A. GHIORSO, S. G. THOMPSON, K. STREET, and G. T. SEABORG, *Phys. Rev.* **81**, 154 (1951).
[2] S. G. THOMPSON, Private communication.
[3] D. WALKER and J. H. FREMLIN, *Nature* **171**, 189 (1953).
[4] R. A. GLASS, *J. Amer. Chem. Soc.* **27**, 807 (1955).

Ion	Target radius (cm)	Number of runs	Yields (α-emitting atoms)		$\frac{Cf^{244}}{Cf^{243}}$	Approx. number of C ions per atom of Cf^{245}
			Cf^{244}	Cf^{243}		
C^{12}	58	1	28,000	9,000	$3{\cdot}2 \pm 0{\cdot}3$	1×10^{10}
C^{12}	65	3	27,000	11,400	$2{\cdot}35 \pm 0{\cdot}15$	5×10^{9}
C^{13}	57	2	22,400	1,240	$18 \pm 1{\cdot}5$	5×10^{9}
C^{13}	64	3	73,000	6,200	$11{\cdot}6 \pm 0{\cdot}7$	1×10^{9}

The numbers and ratios quoted refer only to californium atoms decaying by α-emission. Electron-capture decay, which is certainly appreciable in Cf^{245}, was not studied, but this does not affect the conclusions drawn, since it merely introduces an unknown proportionality constant between the absolute and measured ratios.

The estimated errors are not very reliable, as the number of experiments was small. These errors are almost entirely due to variation of cyclotron conditions during each bombardment.

Firm conclusions can, however, be drawn from the differences between C^{12} and C^{13} bombardments. The extra neutron in C^{13} gives a practical gain of almost five times in the relative yield of the longer-lived isotope, Cf^{246}. In the production of elements higher than californium, the importance of producing the heaviest and longest-lived isotope possible is, of course, very great. It is believed that this is the first quantitative measurement of the advantage given by an extra neutron in the bombarding particle.

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The Raman Spectrum and the Structure of the Aqueous Silicate Ion

(*Received* 2 *December* 1955)

The Raman spectrum of the silicate ion in aqueous solution has been investigated. There appear four lines of low intensity: 448 cm^{-1} (50), 607 cm^{-1} (65), 777 cm^{-1} (55), and 935 cm^{-1} (70). The numbers in parentheses are the widths at half-height in cm^{-1}. These are average values which have been obtained from the spectra of many solutions containing mixtures of sodium silicate and sodium hydroxide.

Three possible structures were considered: planar SiO_3^{--}, octahedral $Si(OH)_6^{--}$, and tetrahedral $H_2SiO_4^{--}$. Silicon in silicate crystals has been found in tetrahedral co-ordination with oxygen; however, octahedral co-ordination is reported in SiP_2O_7.[1] The SiO_3^{--} structure can be discarded on both chemical (improbable co-ordination number) and spectral (three lines predicted) grounds. Three analogues were chosen for $Si(OH)_6^{--}$; in all cases, three lines occurred as predicted for an octahedral configuration. Fluosilicate ion[2] has lines at 403, 466, and 646 cm^{-1}; PF_6^- (see Fig. 1) at 456, 578, and 750 cm^{-1}; aqueous[3] $Te(OH)_6$ at 345, 619, and 644 cm^{-1}. The $Si(OH)_6^{--}$ structure probably can be eliminated, because the spectral patterns of its analogues differ from the spectrum obtained for silicate. As may be seen in Fig. 1, the silicate spectrum appears similar to, but somewhat more diffuse than, the spectrum of the closest structural analogue of $H_2SiO_4^{--}$, $H_2PO_4^-$, which has[4]

[1] L. Pauling, *The Nature of the Chemical Bond*, Cornell University Press, Ithaca, N.Y., 1948, p. 382.
[2] J. P. and L. C. Mathieu, *J. Chim. Phys.* **49**, 226–237 (1952).
[3] J. Gupta, *Indian J. Phys.* **12**, 223–232 (1938), and references therein.
[4] A. Simon and G. Schulze, *Z. anorg. allg. Chem.* **242**, 333 (1939).

lines at 401, 511, 885, and 1050 cm^{-1}. The spectral lines of the silicate ion also form a similar pattern to that formed by the stronger lines of molecular sulphuric acid;[5] some further spectral detail is found in the latter case as a result of the sharpness of the lines and of the higher concentration obtainable.

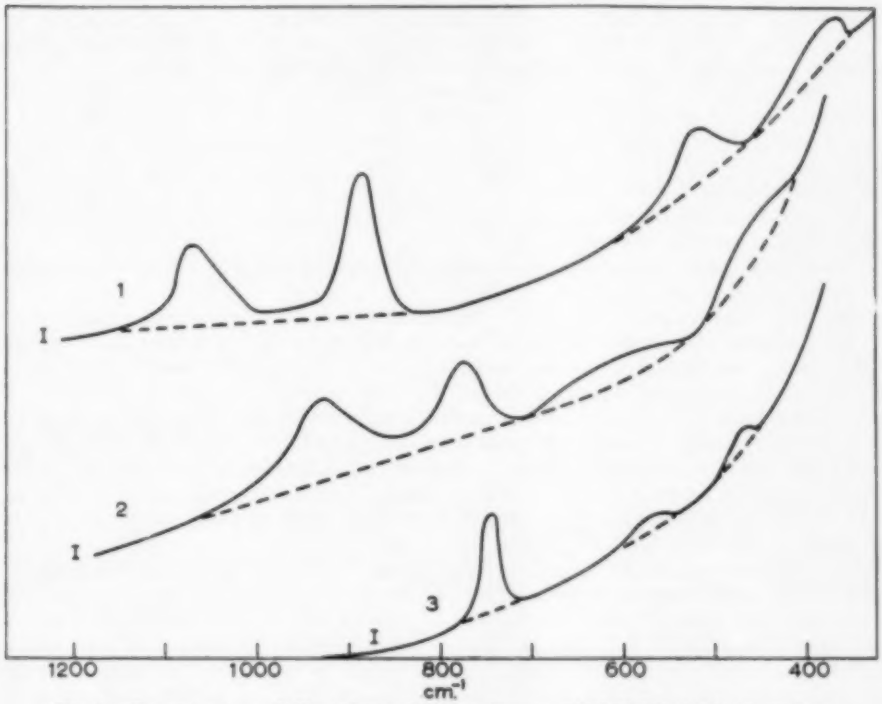

FIG. 1.—Raman spectra of silicate ion and two analogues: (1) NaH_2PO_4 (4 M), (2) sodium silicate (2·5 M) with NaOH (4 M), (3) KPF_6 (saturated). Broken lines and vertical bars represent background levels and noise levels respectively.

On the basis of the above evidence, it is concluded that the aqueous silicate ion has the $H_2SiO_4^{=}$ structure. We should like to emphasize that the observed number of Raman lines does not correspond to the theoretical number for any reasonable structure of the silicate ion. It is only by comparison with the spectra of established structures that it seems possible to resolve the structure of the aqueous silicate ion. Details and other related spectra will be published later.

According to the data of ILER[6] and ROLLER and ERVIN,[7] concentrated silicate solutions mainly contain a dinegative monomeric ion in large percentage and a trinegative dimeric ion which will depolymerize to the monomeric ion upon addition of base. In the spectra of sodium silicate solutions to which little or no sodium hydroxide was added, a fifth line, tentatively attributed to the dimeric silicate ion, was observed at 1040 cm^{-1}. This line decreases in intensity and the 935 and 777 cm^{-1} lines sharpen and increase in intensity when the solutions are made one or two molar in sodium hydroxide.

Acknowledgement—We are grateful to Prof. D. F. HORNIG for a stimulating discussion on this problem.

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A New Method for Producing Perchloryl Fluoride (ClO_3F)

(*Received* 22 *December* 1955)

ONE published method for the preparation of ClO_3F has been the electrolysis of sodium perchlorate in anhydrous hydrofluoric acid.[1] A second method, the fluorination of potassium chlorate, was first investigated by BODE and KLESPER,[2] with the formation of perchloryl fluoride being recognized later by ENGELBRECHT.[3] Both methods give low yields and are hard to control.

We have found that perchloryl fluoride can be made in a smooth reaction from perchlorates and fluosulphonic acid. Numerous experiments were performed both on a small scale and on a scale which allowed the production of many pounds of perchloryl fluoride in one run. This method allows the preparation of perchloryl fluoride from readily available, inexpensive raw materials, since technical-grade chemicals can be used. The purity of the perchloryl fluoride produced via this method was determined by infra-red and mass-spectrographic analysis. About 1% air, 0·4% CO_2 (and no other impurities) were found.

The reaction can be carried out in glass laboratory equipment, and we have used this material over a long period of time without any difficulty.

The following procedure is convenient for the laboratory preparation of perchloryl fluoride:

10 g potassium perchlorate, dissolved in 100 g fluosulphonic acid,[4] is charged into a 250-ml flask equipped with stirrer, thermowell, and reflux condenser. While the mixture is slowly stirred, the temperature is raised. At about 50°C, perchloryl fluoride starts to be evolved and is passed over a solution of aqueous 10% sodium hydroxide containing sodium thiosulphate (5%), and then bubbled through such a solution. The scrubbed gases are passed over solid potassium hydroxide and condensed in a trap cooled with liquid oxygen. The reaction proceeds rapidly around 85°C, and the product is finally swept out of the system with dry nitrogen. The reaction mixture stays liquid at all times. About 5 g of pure perchloryl fluoride (67% of theory, based on potassium perchlorate) are produced this way.

When potassium perchlorate is heated in fluosulphonic acid, characteristic colour changes occur. The solution, at first colourless, becomes yellow, orange, dark brown, red, then orange, yellow, and again colourless. These changes are believed to be caused mainly by $(ClO_2)_2S_2O_{10}$. It is known that compounds of similar type can be formed from chlorine dioxide and sulphur trioxide.[5] $(ClO_2)_2S_2O_{10}$, which is of deep-red colour, decomposes without any danger of explosion at temperatures higher than 85°C into chlorine, oxygen, and sulphur trioxide. The formation and subsequent harmless decomposition of this compound, therefore, seems to prevent the build-up of chlorine oxides, decomposing them innocuously into chlorine, oxygen, and sulphur trioxide, the latter being refluxed back into the system.

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The Reaction of Aluminium Borohydride and Trimethylchlorosilane

(*Received 11 November* 1955)

As part of an exploratory study* to investigate the possibility of forming hydrogen compounds containing boron and silicon in the same molecule, we have found that sodium and potassium borohydrides ($NaBH_4$ and KBH_4) are quite inert to trimethylchlorosilane, $(CH_3)_3SiCl$, at pressures

* Ph.D. thesis of NEIL C. GOODSPEED, submitted to the Graduate College of the State University of Iowa, January 1956.

below atmospheric, at temperatures up to about 130°C, and in the absence of other substances. Aluminium borohydride, $Al(BH_4)_3$, however, reacts very readily. In the presence of excess chloride, essentially all the boron of the borohydride was released as diborane, B_2H_6, as confirmed by vapour-tension measurements and quantitative hydrolysis. All the aluminium was found to remain in that part of the product which was nonvolatile at 25°C. The aluminium borohydride was completely consumed, and, for each mole, three moles of trimethylchlorosilane were consumed and three moles of a fraction intermediate in volatility between diborane and aluminium borohydride were formed. Except for some hydrogen, no other volatile products were observed. The intermediate fraction was found through vapour-density determination to have an average molecular weight of 74·0 (theoretical value for $(CH_3)_2SiH$, 74·1). It was resistant to hydrolysis by water, but with alcoholic KOH[1] yielded 1·1 mole of H_2 per mole (theoretical value for $(CH_3)_2SiH$, 1·0). Pyrolysis formed a black deposit, which when chlorinated and then hydrolysed gave abundantly a white insoluble solid resembling silica. The fraction thus appeared to be trimethylsilane.[2] The stoichiometry suggests that the major reaction may be represented by the following equation:

$$2Al(BH_4)_3 + 6(CH_3)_2SiCl \rightarrow Al_2Cl_6 + 3B_2H_6 + 6(CH_3)_2SiH.$$

Nevertheless, the "trimethylsilane" fraction was tensiometrically inhomogeneous. We were unable to fractionate it into pure compounds, but by careful control of distillation time and temperature, separated it into three fractions, each nearly homogeneous. About two-thirds was in the middle fraction *B*, and one-sixth each in the more *A* and less *C* volatile fractions. Data for these fractions are summarized in Table 1.

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TABLE 1.—DATA ON FRACTIONS FROM "TRIMETHYLSILANE"

	mol. wt.	active H/mole
Fraction *A*	58·6	2·07
$(CH_3)_2SiH_2$	60·1	2·00
Fraction *B*	74·0	0·91
$(CH_3)_2SiH$	74·1	1·00
Fraction *C*	85·8	0·08
$(CH_3)_4Si$	88·1	0·00

Evidently the "trimethylsilane" fraction formed by the reaction of aluminium borohydride with trimethylchlorosilane is actually chiefly a mixture of dimethylsilane (b.p. −20°C),[3] trimethylsilane (b.p. 9°C),[2] and tetramethylsilane (b.p. 27°C).[4] The nature of the mechanism of rearrangement, or disproportionation, thus indicated, is not established. However, it is interesting that similar reactions of a number of other silicon compounds have been reported.[5] The conditions have in all cases been more severe than in the present investigation, but, in several instances,[6] aluminium chloride appeared to act as catalyst.

The reaction between aluminium borohydride and trimethylchlorosilane was studied mainly in the vapour phase at 25°C, but even at −80°C, where both reactants are only very slightly volatile solids, diborane is released rather rapidly. Evidently, either no intermediate silicon borohydride is formed in the reaction or it is extremely unstable. This result is consistent with the observation[7]

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that the BH_3 group appears to become stable associated with combined hydrogen, forming a borohydride (BH_4) group, only when the partial charge[8] on that hydrogen is more negative than that of hydrogen in diborane (or the BH_2 group). According to this observation, a stable $Si(BH_4)_4$ would seem unlikely, since the charge on hydrogen in silane is only −0·053 (electron); not very different from that on hydrogen in diborane, −0·048. In trimethylsilane, the likelihood of a stable association with BH_3 seems even less, as the partial charge on hydrogen in this silicon compound is only −0·007.

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J. Inorg. Nucl. Chem., 1956, Vol. 2, pp. 269 and 270. Pergamon Press Ltd., London

(p, He^3) AND (p, t) CROSS-SECTION MEASUREMENTS

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(*Received* 8 *December* 1955)

Abstract—Results are given for some recent measurements of (p, He^3) and (p, t) cross-sections. The results indicate no need for a sizable many-body correction in computing probabilities for emission of He^3 and triton nuclei.

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INTRODUCTION

One of the basic assumptions of the statistical theory of nuclear reactions[1] is that the compound nucleus emits all possible types of particles with equal probability, except for energetic and Coulomb differences. Thus, naively, the compound nucleus would be expected to decay in a great variety of ways, yielding all possible pairs of nuclei that can be formed from the constituent nucleons. Energetic considerations greatly simplify this naive picture; for a given excitation of the compound nucleus, conservation of energy eliminates all but a few of the many possible pairs of nuclei. Thus, for example, for the bombardment of middle Z elements at energies below about 6 MeV the only possible reaction products are usually protons, neutrons, and alphas, each paired with its corresponding residual nucleus. As the bombarding energy is increased, additional reaction products become energetically possible, and the hypothesis of equal probability for all possible particles can then be tested more stringently. The first such new-reaction products to appear are the H^2, H^3, and He^3 nuclei, which (again for the middle Z region) typically become energetically possible at about 7-, 12-, and 13-MeV bombarding energies, respectively. For bombarding protons, reactions leading to deuteron emission are known to proceed quite frequently by noncompound nucleus mechanisms, and hence do not afford a fair test of the equal-probability hypothesis. On the other hand, for (p, t) reactions, the experimental angular distributions observed by Cohen and Handley[2] indicate a compound nucleus process, except perhaps for certain special shell configurations of the target nucleus. Likewise for (p, He^3) reactions, it seems intuitively quite unlikely that anything except a compound-nucleus process could contribute substantially to the reaction. Hence, observations of (p, t) and (p, He^3) cross-sections constitute a test of the equal-probability hypothesis. The present paper describes the results of several such measurements.

EXPERIMENTAL METHOD

Measurements were made of the (p, He^3) cross-section of Ga^{71} and of the (p, t) cross-section of Cu^{63}. Also, upper limits were observed for the (p, He^3) cross-sections of Ca^{40} and Ca^{44}. The measurements were made by activation methods in the internal circulating beam of the ORNL 86-inch cyclotron. Beam current was measured by comparing the activity from the cross-section to be

* Operated by Union Carbide Nuclear Company for the U.S. Atomic Energy Commission.

[1] Blatt and Weisskopf, *Theoretical Nuclear Physics*, John Wiley and Sons.

[2] B. L. Cohen and T. H. Handley, *Phys. Rev.* **93**, 514 (1954).

measured with that resulting from a known cross-section. After the bombardment, chemical separations were performed on all samples, to remove unwanted activities resulting from transmutation reactions. The decay of the radioactive-product nuclei was observed under end-window counters, and the decay curves were analysed graphically to find the intensity of the various component half-lives. Known decay-scheme information[3] was then used to convert the intensities into cross-sections.

RESULTS

The experimental results which were obtained are shown in Table 1. The $\approx$ sign may be taken to mean that the result is uncertain by as much as a factor of 3. The (p, t) cross-section of Fe^{54} was taken from the previous work of Cohen and Handley.[2]

Table 1.

Reaction	Target	Bombarding energy (MeV)	Thresholds (MeV)	Cross-sections (mb)
(p, He^3)	Ca^{40}	22·4	13·4	$\lesssim 2$
	Ca^{44}	22·4	14·5	$\lesssim 1$
	$Ga^{71} \rightarrow Zn^{69}$	22·4	9·4	$\approx 0{\cdot}05$
	$Ga^{71} \rightarrow Zn^{69*}$	22·4	9·8	$\approx 0{\cdot}05$
(p, t)	Cu^{63}	20·0	10·3	$2{\cdot}2 \pm 0{\cdot}8$
		22·4	10·3	$3{\cdot}5 \pm 0{\cdot}9$
	Fe^{54}	19·0	15·0	0·004
		22·4	15·0	0·200

The results give an indication of the general order of magnitude which may be expected from reactions of this type. Comparison of the relative probability of triton and He^3 emission to that of neutron and proton emission can best be made by assuming threshold and barrier penetration effects to be adequately described by the statistical theory of nuclear reactions.[1] It is then found that the experimental results are in order-of-magnitude agreement with the calculated cross-sections, where the calculations were performed by using approximate correction factors for the differences in penetration and density of states of the triton and proton, and likewise of the He^3 and alpha particle. It then seems reasonable to conclude, within the limits of the experimental sampling, that deviations from the equal-emission probability hypothesis must be generally less than an order of magnitude. This result is in sharp contrast with the prediction of the many-body theory of alpha decay[4, 5], according to which emission of tritons or He^3 nuclei should be inhibited by many orders of magnitude. Thus, the results of this experiment strongly support the equal-emission hypothesis as contrasted with the many-body theory of alpha decay.

[3] Seaborg, Hollander, and Perlman, *Rev. Mod. Phys.* **25**, 469 (1953).
[4] H. A. Bethe, *Rev. Mod. Phys.* **9**, 161 (1937).
[5] B. L. Cohen, *Phys. Rev.* **80**, 105 (1950).

J. Inorg. Nucl. Chem., 1956, Vol. 2, pp. 271 to 285. Pergamon Press Ltd., London

THE SLOW-NEUTRON ABSORPTION CROSS-SECTION OF 9·2-H Xe^{135} BY THE METHOD OF NEGATIVE ACTIVATION*

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(*Received* 29 *November* 1955)

Abstract—The absorption cross-section of 9·2-h Xe^{135} for thermal (pile) neutrons has been measured in three experiments, using two variants of the method of negative activation. The value obtained is $2{\cdot}58 \pm 0{\cdot}20 \times 10^{-18}$ cm²/atom for a mean neutron temperature of 400° K in a reactor moderated by heavy water.

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INTRODUCTION

ANOMALIES were observed in the operation of the first high-powered uranium pile in this country. From the kinetic behaviour of the pile reproduction constant these were interpreted as arising from poisoning by the fission product 9·2-h Xe^{135}. From the magnitude of the poisoning effect, the absorption cross-section of Xe^{135} was calculated to be 3·3 megabarns,[1] on the assumption that the fission yield was 5·9%. Pile behaviour determines essentially only the product of fission yield and absorption cross-section.

These results were checked by similar experiments on the graphite pile at the Oak Ridge National Laboratory and on the heavy-water pile of the Metallurgical Laboratory in Chicago. The Oak Ridge experiment[2] indicated an absorption cross-section for Xe^{135} of $2{\cdot}7 \pm 0{\cdot}4$ megabarns for a yield of 5·9%. The Metallurgical Laboratory (now Argonne National Laboratory) experiment[3] gave a value of 1·9 megabarns for a fission yield of 5·9%, with a very large indicated uncertainty.

It was deemed desirable to confirm the assignment of the poisoning to 9·2-h Xe^{135} by more direct experiments involving the separated fission product. In addition, such measurements would give values for the absorption cross-section independent of the fission yield.

The experiments described herein were performed in the period 1944–1945.

PRINCIPLE OF EXPERIMENTAL METHOD

Several methods for determining the cross-section of Xe^{135} have been considered, none of which involves the assumption of a value for the fission yield. The measurement of the effect on the reactivity of a pile by introduction of known amounts (~100

* Based on work performed under the auspices of the U.S. Atomic Energy Commission and on reports CP-2620, CP-2782, and ANL-4886.

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[1] 1 megabarn = 10^{-18} cm²/atom.

[2] L. B. BORST, H. JONES, L. W. NORDHEIM, L. SLOTIN, and H. SOODAK *Metallurgical Laboratory Report* CP-2192.

[3] W. H. ZINN *Metallurgical Laboratory Report* N-1610 October 3, 1944; E. FERMI, W. H. ZINN, and associates *Metallurgical Laboratory Report* CP-2301 October 28, 1944.

curies) of Xe^{135} (danger-coefficient method) and the determination of the attenuation of a slow-neutron beam by a sample of Xe, both involve handling very active sources. Of the other methods, most involve the radiochemical assay of samples for xenon or its active daughters by radiation measurements. A brief survey of the properties of the fission decay chain of mass number 135 at this point will be of later use.

The presently (1956) accepted scheme for the decay chain of mass number 135 as it is formed in the fission of uranium with pile neutrons is given as:

$$\begin{array}{l} <\text{2-min } Te^{135} \rightarrow \text{6·7-h } I^{135}(70\%) \rightarrow \text{9·2-h } Xe^{135} \rightarrow 3{\cdot}0 \times 10^6\text{-yr } Cs^{135} \rightarrow \text{stable } Ba^{135}. \\ \qquad\qquad\qquad\qquad\qquad\qquad\quad \uparrow \quad \text{I·T} \\ \qquad\qquad\qquad\qquad\qquad\qquad (30\%) \rightarrow \text{15·6-min } Xe^{135m} \end{array}$$

The 9·2-h Xe^{135} is formed independently in the fission process to the extent of 0·3% fission yield;[4] the total yield of the Xe^{135} is 6·25%.[5] The 15·6-min xenon isomer formed to the extent of 30%[6] in the decay of 6·68-h. I^{135} has been shown[7] to decay by isomeric transition to 9·2-h xenon. The 9·2-h xenon emits betas of 0·90 MeV[8] maximum energy and 0·25 MeV gammas.

At the time of these experiments the radiations of the long-lived Cs^{135} isotope had not yet been observed. It is now known[9] to decay with a beta of 0·21 MeV with a life-time of 3×10^6 y.

Samples of 9·2-h Xe^{135} prepared from uranium fission will also contain 5·3-day Xe^{133} activity, associated with the chain.

$$\begin{array}{l} \text{4·4-min } Sb^{133} \rightarrow \text{2-min } Te^{133} \rightarrow \text{20·8-h } I^{133} \rightarrow 97{\cdot}6\% \text{ 5·3-day } Xe^{133} \rightarrow \text{stable } Cs^{133}. \\ \qquad\qquad\quad \searrow \quad\quad \uparrow \qquad\qquad\qquad\qquad\qquad\quad \searrow \quad\quad \nearrow \\ \qquad\qquad\quad \text{63-min } Te^{133m} \qquad\qquad\qquad\qquad\qquad\quad 2{\cdot}4\% \text{ 2·3-day } Xe^{133} \end{array}$$

Also it is known today that 12-day Xe^{131} will be present in small amounts.

Several krypton activities may also be present in mixtures of rare-gas fission products, most importantly 3-h Kr^{88} and 4·7-h Kr^{85}.

Two types of experiments have been tried in which the cross-section of the 9·2-h Xe^{135} is deduced from the diminution of its radioactivity upon exposure to a high-neutron flux. The two types differ essentially in the order in which the preparation of the 9·2-h Xe^{135} sample for assay and the irradiation of the Xe^{135} with neutrons is made.

One method, suggested by Prof. E. WIGNER, consists in the simultaneous irradiation of two samples of uranium, one in the centre of the pile in the region of highest flux, and the other and much larger sample at the periphery where the flux is, say, tenfold smaller. At saturation, the rate of formation of the Xe^{135} is equal to the rate of its disappearance by beta-decay plus removal by neutron-capture

$$FY = (\lambda + n v \sigma_c)N, \qquad (1)$$

where F = fission rate, Y = fission yield, λ = decay-constant of 9·2-h Xe^{135}, nv =

[4] E. J. HOAGLAND and N. SUGARMAN *NNES* Vol. 9 (McGraw-Hill Book Company, Inc., New York, 1951) p. 1035; F. BROWN and L. YAFFE *Canad. J. Chem.* **31**, 242 (1953).
[5] E. P. STEINBERG and L. E. GLENDENIN *Survey of Radiochemical Studies of the Fission Process* to be published in Proceedings of the Geneva Conference (1955).
[6] W. C. PEACOCK, A. R. BROSI, and A. D. BOGARD *Oak Ridge National Laboratory Report* ORNL-176 (1948).
[7] C. S. WU and E. SEGRE *Phys. Rev.* **67**, 142 (1945).
[8] I. BERGSTROM *Phys. Rev.* **82**, 112 (1951).
[9] N. SUGARMAN *Phys. Rev.* **75**, 1473 (1949).

neutrons/cm² sec, σ_c = capture cross-section of the poison, and N = number of atoms of Xe^{135}.

For a neutron flux ca. 10^{12} neutrons/cm²/sec (about that obtaining for the centre of the Argonne heavy-water pile, CP-3), and for a cross-section of ca. 3×10^{-18} cm², the rate of removal by capture, $nv\sigma_c$, is ca. 15% of the beta-decay rate. For a flux of ca. 10^{11} (edge of the pile), the capture effect would only amount to ca. 1·5%, so that the equilibrium ratio of the number of Xe^{135} atoms (and hence of the beta activities) of the two samples, per fission, should differ from unity by ca. 13%. The details of such an experiment are given below, in Section Experimental 1.

A second "depletion" method for determination of the cross-section of 9·2-h Xe^{135} was suggested by ELLIOTT and co-workers[10] of Clinton Laboratories (now Oak Ridge National Laboratory). The method consists of the determination of the diminution of the activity of a sample of 9·2-h Xe^{135} which has been exposed to a high-neutron flux compared to a similar unexposed sample. The 9·2-h xenon is most conveniently prepared as a fission product.

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In a sample of fission-product xenon activity, the 9·2-h Xe^{135} will decay exponentially,

$$A = A_0 e^{-\lambda t}. \tag{2}$$

If a portion A'_0 of this Xe^{135} be irradiated with thermal neutrons in a flux nv for a time t, its activity at time t will be

$$A' = A'_0 e^{-(\lambda + nv\sigma_c)t} \tag{3}$$

where σ_c is the thermal neutron capture cross-section of the 9·2-h Xe^{135}. Comparing activities of the bombarded and unbombarded gases at time t:

$$A/A' = (A_0/A'_0)\,(e^{nv\sigma_c t})$$

or

$$\sigma_c = [\ln (A/A' \times A'_0/A_0)]/nvt = \ln P/nvt. \tag{4}$$

P is thus the "depletion factor" of the bombarded gas.

Since both the irradiated and control samples decay with the same period after the irradiation, the ratio A/A' is independent of time of decay after bombardment, and so may be measured at any time within the limitations of the amount of 9·2-h Xe activity available. From the ratios of the 9·2-h xenon activities of the two samples before and after bombardment and from the neutron flux and time of irradiation, the value of the cross-section can be calculated.

This method has some advantages over the Wigner "two-flux" method described above. The magnitude of the depletion effect may be increased without limit in the Elliott experiment by increasing the duration of the bombardment, whereas in the "two-flux" method the ratio of the 9·2-h Xe^{135} activities in the two samples asymptotically approaches a maximum value of

$$R = (\lambda + nv\sigma_c)/\lambda. \tag{5}$$

Moreover, this ratio begins to decrease as soon as the bombardment ceases, because of the "dilution" of the irradiated 9·2-h Xe with unirradiated 9·2-h Xe which grows into the sample from its 6·7-h I parent. Thus, for a 40-h bombardment, the observed depletion amounted to only ca. 2·5% in the "two-flux" method, whereas in an

[10] N. ELLIOTT, J. D. KNIGHT, T. B. NOVEY and E. SHAPIRO, unpublished work.

experiment of the Elliott type, a 15-h bombardment gave observed depletion of 21%. The Elliott experiment, moreover, requires only one flux measurement; the Wigner experiment requires two. An additional difficulty in the Wigner experiment is the necessity for precise timing of the instant of final removal of the xenon from the dissolved uranium, and of the necessity for complete removal and perfect mixing of all the xenon evolved from the solution before that time. This requirement follows from the necessity for correcting for the fraction of xenon which grew in from the iodine parent between the end of the bombardment and the time of removal of the xenon activity from the iodine activity. The relative disadvantages of the Elliott method will appear in the descriptions of the individual experiments (see below).

Three experiments on the xenon cross-section measurement by the negative activation method are reported in this paper. The results of these and other experiments are compared in the final section of this paper.

EXPERIMENTAL

Wigner "Two-flux" Experiment

This experiment was attempted as a first effort to measure σ_c by members of the Fission Product Section of the Metallurgical Laboratory.[11] The experiment employed the Wigner "two-flux" method described above. One 10-g piece of uranium foil, sealed in a welded aluminium capsule, was bombarded for 40 h in the central vertical thimble of the heavy-water pile at the Metallurgical Laboratory (nv = ca. 10^{12} neutrons/cm^2/sec). Concurrently, a 50-g piece of uranium, similarly sealed, was irradiated in the thermal column of the pile next to the reflector where the flux is about 10^{11}. A larger piece is used in the lower flux position, so that comparable activities of xenon from the two samples are available for radiochemical assay.

After irradiation, the pieces were dissolved in HCl as rapidly as possible, jacket and all, in each of two identical shielded glass vacuum systems. As soon as the irradiation in the pile ceases, the Xe^{135} in the metal begins to be "diluted" by unexposed Xe^{135} which grows in from its 6·7-h I parent, so rapid removal of the exposed xenon from the I^{135} is desirable, since the freshly formed Xe^{135} diminishes the apparent effect. Therefore, the dissolution was hurried to completion within two to three hours.

Xenon was carefully separated from the solution of both samples and from other gaseous activities, placed in gas counting cells, and the radioactivity of the two compared as a function of time on our atmospheric-pressure ionization chamber with an FP54 electrometer amplifier, using null-method detection. A 42-mg copper absorber was used on both samples to emphasize the contribution of the 9·2-h Xe^{135} as compared to the 5·3-day Xe^{133} by ca. one hundredfold.

Since presumably the Xe^{133} does not have a cross-section high enough to deplete it significantly at those fluxes,[12] it can be used as a monitor for the transfer of the xenon activities from the uranium slug to the counting cells (this transfer is far from quantitative). Because of the unequal destruction of the 9·2-h xenon in the two samples during the bombardment, the 9·2-h xenon component of the higher flux sample is less than that of the lower flux sample relative to the 5·3-day Xe^{133}. Thus, when one normalizes the decay curves for the samples from high and low flux to the 5·3-day xenon, a comparison of the 9·2-h Xe^{135} curves gives the desired effect. Initially the ratio is constant, since the 9·2-h xenon is the major activity in the sample. Later, after the decay of the 9·2-h xenon, the ratio is again constant, but higher than before. The difference in the ratios is a measure of the cross-section of the 9·2-h xenon.

The ratio must be corrected for the amount of "unexposed" Xe^{135} which grows into the sample after removal from the pile and before dissolution, and for the relative counting efficiencies of the counting cells for the two different isotopes. The flux to which the samples were exposed was determined by radiochemical assay of the uranium solutions for 12·8-day Ba^{140}.

[11] M. S. FREEDMAN, R. M. ADAMS, A. TURKEVICH, N. SUGARMAN, and S. RAYNOR *Metallurgical Laboratory Report* CS-2281 (Oct. 17, 1944).

[12] Recent work at Argonne National Laboratory has established an upper limit on the neutron capture cross section of Xe^{133} of a few thousand barns: E. P. STEINBERG, L. E. GLENDENIN, M. G. INGHRAM, and R. HAYDEN, ANL-OCS-269 (to be published). Also see reference 5.

The inconsistencies in the cell calibration, persisting throughout two lengthy experiments, rendered the results of this "Wigner type" determination inconclusive. An absorption cross-section for 9·2-h Xe^{135} of 2·5 megabarns is consistent with the data from these experiments. Further work was concentrated on the Elliott type of experiment, in which an isolated 9·2-h Xe^{135} sample was exposed to neutrons and the destruction measured.

Elliott-type Depletion Experiments

Four experiments of the Elliott type were carried out by members of the Clinton Laboratories and of the Metallurgical Laboratory. The several experiments differ as to the techniques used for measuring the 9·2-h Xe^{135} activity relative to the 5·3-day Xe^{133} activity, for determining the flux, for preparing the sample, and for determining the efficiency with which the 9·2-h Xe is transferred, i.e. for ensuring that the changes in the 9·2-h Xe activity are due only to decay and to neutron capture.

EXPERIMENT No. 1[13]

A 15-g sample of uranyl nitrate hexahydrate was irradiated in the centre of the heavy-water pile at the Metallurgical Laboratory for 10 min, ($nv \approx 10^{12}$ neutrons/cm²/sec). Two hours after the end of bombardment, iodine activity was extracted from the dissolved uranium salt and was placed in a small vacuum system (as a basic iodide solution). The system was evacuated, the solution was degassed by boiling, and it was allowed to stand at room temperature for six hours to grow in 9·2-h Xe^{135}. At the end of this time the solution was boiled under vacuum, a small amount of carefully purified helium (used as a carrier gas) was passed through the solution to sweep out the xenon gas, and the active xenon-helium mixture was transferred by means of a Toepler pump into a glass storage bulb.

Analysis of the gross decay-curve of a sample of this stock gas indicated that it was very pure 9·2-h Xe^{135}. Thirty-one hours after preparation (twelve hours after the end of the gas irradiation), the activity was still 98% Xe^{135}. The rest was 5·3-day Xe^{133}.

Four quartz tubes of about 30-cc volume were filled from the stock bulb and sealed off. Two of these (Nos. 1 and 5) were placed at the bottom of the "thimble" of the heavy-water pile (CP-3), in the position of greatest neutron intensity. Another one (No. 6) was placed several feet higher up in the thimble in a region of low-neutron flux. These gas samples received an irradiation of 13·68 h with the pile operating steadily at full power. The last sample (No. 4) received no radiation at all.

The gas-counting cells used in this experiment were brass cylinders of 1·5 cm i.d. and about 2·5 cc volume. They were silver-soldered to brass cards which fit into a standard shelf arrangment under a thin mica-window Geiger-Muller tube in a lead shield. The cell windows were made of 42 mg/cm² phosphor bronze soft-soldered over the openings of the cylindrical cells. The gas was transferred into the cells through a narrow copper tube fitted with a small glass stopcock.

While the gas in the quartz tubes was being bombarded in the pile, some counting cells were filled in pairs by means of a Toepler pump to a fixed pressure with the 9·2-h Xe^{135} activity from the storage bulb. These pairs of cells were counted a number of times on the top shelf of a standard G-M tube arrangement. The ratio of the counts of 9·2-h Xe^{135} for each pair of cells, after correction for the small decay occurring between the counts on each cell, constitute a measure of the relative counting efficiencies of the cell pair for the 9·2-h Xe^{135} activity.

After the pile bombardment of the gas in the quartz tubes, the counting cells were emptied of the stock gas and refilled in the following manner: one of each matched pair of cells was filled again with the stock gas and the other was filled to the same pressure from one of the bombarded quartz tubes. The cell pairs were counted again and the relative counts, when corrected for the relative counting efficiencies of the cells, determined the ratio A/A' of equation (4).

Table I summarizes the results obtained for the ratios of equation (4) and illustrates their precision. Each of the ratios quoted represents the mean of at least eight counting determinations. The errors indicated are the average deviations of these determinations.

The neutron flux was determined from weighed uranium monitors sealed in quartz vials and irradiated inside the same bulbs at the same time as the bombarded gas. A radiochemical

[13] R. M. Adams, L. G. Stang, jr., and A. Turkevich *Metallurgical Laboratory Report* CP-2620 (Jan. 12, 1945).

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determination[14] of the 12·8-day Ba^{140} activity produced by fission in this sample was used together with the known fission cross-section and the fission yield of the barium activity (6·1%)[14] to get the neutron flux. The values obtained were $1{\cdot}16 \times 10^{12}$ and $1{\cdot}19 \times 10^{12}$ neutrons/cm²/sec for the two samples at the bottom of the thimble, and $0{\cdot}026 \times 10^{12}$ for the sample several feet up in the thimble.

The correction for resolving time-losses in counting the barium samples on a G-M tube (ca. 9000 c/min) and the correction for fast fission in the uranium would act in opposite directions to extents estimated at about 3%, and so were neglected in this calculation. It is felt that this neutron-flux determination is good to about ±10% and measures only the thermal neutron flux.

TABLE 1.—CELL RATIOS DETERMINED BY 9·2-H Xe^{135} ACTIVITY

Cell pair	Ratio[a] before bombardment = A_0/A'_0	Ratio[b] after bombardment = A/A'	$(A'_0/A_0)(A/A') = P$	Quartz tube in which gas was irradiated	Neutron flux to which quartz bulb was exposed
A/D	1·065 ± 0·011	0·927 ± 0·007	0·871	No. 1	$1{\cdot}160 \times 10^{12}$
U/Z	0·879 ± 0·006	0·770 ± 0·006	0·876	No. 1	$1{\cdot}160 \times 10^{12}$
W/Y	0·999 ± 0·023	0·880 ± 0·008	0·875	No. 5	$1{\cdot}190 \times 10^{12}$
	1·012 ± 0·012				
V/X	1·018 ± 0·020	1·009 ± 0·009	0·991	No. 6	$2{\cdot}64 \times 10^{10}$
	1·020 ± 0·012				
F/Z	0·916 ± 0·011	0·938 ± 0·007	1·023	No. 4	0

[a] Both cells filled with the same gas. When two figures are given, they represent independent determinations involving refilling of the cells with active gas. A straight average was used in calculating the entry for column 4.

[b] Cells D, Z, Y, and X always had gas from the stock sample. Their mates contained gas subjected to irradiation.

The first three lines of Table 1 indicate that 12–13% of the Xe^{135} was destroyed in a flux of $1{\cdot}17 \times 10^{12}$ neutrons/cm²/sec during the 13·68-h. The fourth and fifth lines show that with a low flux ($0{\cdot}02 \times 10^{12}$ neutrons/cm²/sec) or no bombardment, there is no destruction other than the natural beta decay (within the accuracy of the determination of ca. 2%).

To see if the results were being affected by processes other than destruction by neutrons (for example, by a "clean-up" of the tracer xenon by the walls of the quartz tube), use was made of the Xe^{133} (5·3-day) activity in the bombarded and unbombarded samples of the gas, in the following way.

Several days after the bombardment, when all but the 5·3-day Xe^{133} had decayed, the same cells were refilled to a higher pressure with the appropriate gas samples and the ratios of the counts compared with the ratios when they were both filled with the stock gas. They are summarized in Table 2. Because of the low activities, the determinations were less accurate than in the main experiment, but they rule out any spurious effect greater than a few per cent, which is the error in the determination.

Another possible source of error is the activation of the carrier gas used. A sample of the helium was tested before using. Under neutron bombardment, a 110-min activity was induced, indicating the presence of argon. The amount was calculated to be about 14 p.p.m. It would have given a contribution of a few per cent at the time the first counts were taken in the main experiment. However, before using, the helium was allowed to remain on activated charcoal at liquid-air temperatures for three hours. No contribution from A^{41} could be detected in the decay curves after the bombardment of the gas.

The above experiments, then, establish that a 13·68-h exposure to a flux of $1{\cdot}17 \times 10^{12}$ neutrons/cm²/sec destroys 0·125 of the Xe^{135} (average of three determinations on two samples of irradiated gas). This corresponds to a cross-section of 2·36 *megabarns*. The ratio product P in equation (4) was probably not established to better than 3%, and the neutron flux probably not to better than 10%. Therefore, the 2·36-megabarn cross-section for Xe^{135} was not established to better than 25%.

[14] M. S. FREEDMAN and D. W. ENGELKEMEIR *NNES*, Vol 9 (McGraw-Hill Book Company, Inc., New York, 1951), p. 1344.

TABLE 2.—CELL RATIOS DETERMINED BY 5·3-DAY Xe^{133} ACTIVITY

Cell pair	Ratio[a] when filled with same gas A_0/A'_0	Ratio[b] after bombardment A/A'	$(A'_0/A_0)(A/A') = P$	Neutron flux to which gas was exposed
A/D	1·105 ± 0·012 1·105 ± 0·015 1·100 ± 0·003	1·112 ± 0·030	1·007	$1·160 \times 10^{12}$
U/Z	0·931 ± 0·009 0·918 ± 0·009	0·898 ± 0·041	0·971	$1·160 \times 10^{12}$
W/Y	0·997 ± 0·011	1·015 ± 0·032	1·019	$1·190 \times 10^{12}$
V/X	0·993 ± 0·014	0·956 ± 0·028	0·964	$2·64 \times 10^{10}$

[a] When several figures are listed, they represent different fillings of the cells with the same gas. A straight average of the given figures was used in calculating column 4.

[b] Cells D, Z, Y, and X had the gas from the stock sample. Their mates contained gas subjected to irradiation.

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EXPERIMENT No. 2

Introduction

A later depletion experiment[13] of the Elliott type performed at the Metallurgical Laboratory used sufficiently large activities of 9·2-h xenon to permit the use of an ionization chamber for following the xenon decay, with consequent improvement in the precision of measuring the depletion ratio P of equation (4). Extensive precautions were taken to ensure the elimination of systematic errors concerned with alterations in the 9·2-h xenon activity due to causes other than beta-decay or neutron absorption, to guarantee the accuracy of the measuring amplifier system, to diminish and correct for previously noted variations in counting efficiencies of the cells containing the active gas, to account for other radioactivities produced by the neutron irradiations, and to determine accurately the neutron flux.

In order to avoid the necessity for quantitative total gas transfer into and out of the vessel in which the irradiation was performed, specific activities (activity per unit gas volume at standard conditions) were measured. Possible fractionation of xenon from other carrier gases by such processes as selective absorption or differential diffusion was minimized by the addition of a small quantity of natural xenon as carrier gas. Experience in preliminary experiments gave evidence of the fractionation of xenon activity from nonisotopic carriers, especially during the sealing or transfer operations to the quartz bombardment tube. The neutron-induced activity in the carrier xenon was very small and was corrected for.

As in the other depletion experiments reported here, in this experiment the ratio A'_0/A_0 was determined using the 5.3-day Xe^{133} as a monitor; since it is unaffected by the neutron irradiation,[12] its concentration will be proportional to the total concentration of xenon in the gas.

In preparing sufficient quantities of 9·2-h Xe for the experiment, one obtains an activity of 5·3-day xenon amounting to about 50% of the 9·2-h xenon activity at the time of measuring the ratio A/A'. This long-lived activity would dilute the measured apparent effect $(1 - A'/A)$ and would make difficult the time-corrections to be applied to successive measurements. To maximize the ratio of 9·2-h Xe to 5·3-day Xe, as measured in the ionization chamber, the samples were counted through 84 mg/cm² of copper absorber, sufficient to cut out all the 5·3-day Xe betas and of high specific absorption for the 30 keV X-ray of the 5·3-day Xe. Such an absorber lowered the measured 5·3-day xenon activity by a factor of 300 to 600, and the 9·2-h xenon activity by perhaps four- to six-fold. When A_0'/A_0 was determined after six to eight half-lives of 9·2-h xenon, the Cu absorber was removed and a very good 5·3-day decay was obtained.

It was, of course, necessary to remove other offending activities, such as the kryptons, in preparing

[13] M. S. FREEDMAN, R. M. ADAMS, A. TURKEVICH, and N. SUGARMAN *Metallurgical Laboratory Report* CP-2782 (February 15, 1945); M. S. FREEDMAN *Argonne National Laboratory Report* ANL-4886 (September 12, 1952).

the xenon, or to make the measurements after they had decayed away. Further, since the xenon was carried in large amounts of diluting gases such as helium and other gases not easily removed from xenon (air, NO, etc.), the activities induced by neutron bombardment in these diluents must be known and correction for them must be made. The need for accurate pressure measurements for precise determination of specific activities dictated the use of such large amounts of diluting gas.

The neutron-flux measurements will be discussed in detail below.

Measurement of Depletion Ratio P

A 100-g aluminium-coated uranium cylinder was irradiated for three hours at 300 kW in the "thimble" of the heavy-water pile, CP-3, the sample being cooled with an air-jet during bombardment. The uranium and the aluminium coat were dissolved with 6 N HCl in an all-glass vacuum system under one-half atmosphere of helium. The gas evolved was passed through two cold traps and two scrubbing traps (KOH and $NaHSO_3$) and collected on activated charcoal at dry-ice temperatures. When solution of the slug was complete, the charcoal was warmed, and that portion of gas which could be pumped off with a Toepler pump at room temperature was discarded. Most of the krypton came off at this point. The charcoal was then heated to 360° C, and the desorbed gas was collected. This gas contained the 9·2-h Xe^{135} and 5·3-day Xe^{133} activities.

A small quantity (about $\frac{1}{3}$ cc at N.T.P., or 24 cc at 1-cm pressure) of natural xenon was added to this gas for "carrier," to aid in the separation from the active krypton and to minimize peculiar adsorption or handling effects which we have found in dealing with tracer amounts of xenon. The gas was passed over soda-lime to remove CO_2, and condensed in a trap with liquid nitrogen. Noncondensable gas was removed by Toepler pumping, which also removed about one-third of the gross activity. Next the xenon was evaporated and collected in a glass storage bulb. The total gas volume at this stage was 250 cc-cm and the yield of xenon about 40% of theoretical. Helium, from which argon had been removed by activated charcoal at liquid-nitrogen temperatures, was added as a diluent to make the volume up to 5000 cc-cm.

One-fifth of this gas was sealed into each of three quartz tubes, Nos. 1 and 2 for bombardment and No. 3 as a control. A fourth tube was filled with natural xenon, and sealed. The tubes had been degassed by extensive heating, and tested for leaks. Each of the quartz tubes contained a small (100-mg) piece of uranium sealed in an evacuated quartz vial, and a small gold foil was scotch-taped on the outside of the tubes near each end, both to be used for determining the neutron flux. The rest of the gas was kept in the glass bulb as standard or "master" gas. A small sample of this gas in one of the standard counting cells was followed on the ionization chamber, FP54 amplifier for gross decay (curve *A*, Fig. 1).

Sixteen hours after the bombardment of the uranium for preparation of Xe^{135} the quartz tubes were placed in the thimble of the heavy-water pile (from which all other samples and the cooling water had been removed). A steady 15-h bombardment at full power was run. Bombardment time was measured as 15-h $\pm$ 1 min.

After irradiation, the tubes were attached to the vacuum line with ground joints, the break-off tip of the quartz irradiation cells was broken, and the gas transferred by a Toepler pump to glass storage bulbs. From these bulbs the gas-counting cells were filled on a special vacuum line designed to control and measure accurately filling pressures and temperatures. The cells were Pyrex cylinders, with a flanged top to which a 10 mg/cm² mica window was cemented, and the whole cemented to a brass plate which fitted the shelves of the ion chamber. They were fitted with micro stopcocks and ground joints; their volume of about 5 cc was filled to 17-cm pressure in our experiments. During the filling operation the cells were thermostatted in a water-bath; pressures were read on a differential manometer to 0·1 mm. Prior to each filling, the cells were evacuated, and cell backgrounds, due to adsorbed or otherwise retained activity, were determined. Total corrections due to backgrounds and to filling temperature and pressure variation, amounted to less than 1%.

It is worth noting that in similar experiments using counting cells of brass with copper or steel windows soldered on, in the hope of avoiding adsorption of xenon on glass- or organic-cement surfaces, it proved impossible to maintain calibration ratios between cells stable to within several per cent. This cell instability seems to be associated with adsorption or other retention of xenon activity in the cell which could not be removed by prolonged pumping. This same difficulty was experienced to a much lesser exent with the glass cells, and was further reduced in importance by observing the cell calibrations just before and just after measuring the ratios A/A' and A'_0/A_0.

Two independent methods for measuring the ratios A/A' and A'_0/A_0 were employed. In each, the gases were Toepler-pumped into standard counting cells to a known temperature and pressure. In the first method, two cells of similar construction were filled in parallel with the type of activity (9·2-h Xe or 5·3-day Xe) whose ratio was to be determined, i.e. both cells were open to the line at the same time so as to ensure equality of pressure and temperature in the cells. The ratio of measured activities furnished a relative calibration of the cells for that activity. Next, the cells were filled individually with the two unknown gas samples to closely the same temperature and pressure: the ratio of activities was determined, using the cell calibration. In each of the measurements, corrections for decay between readings were applied.

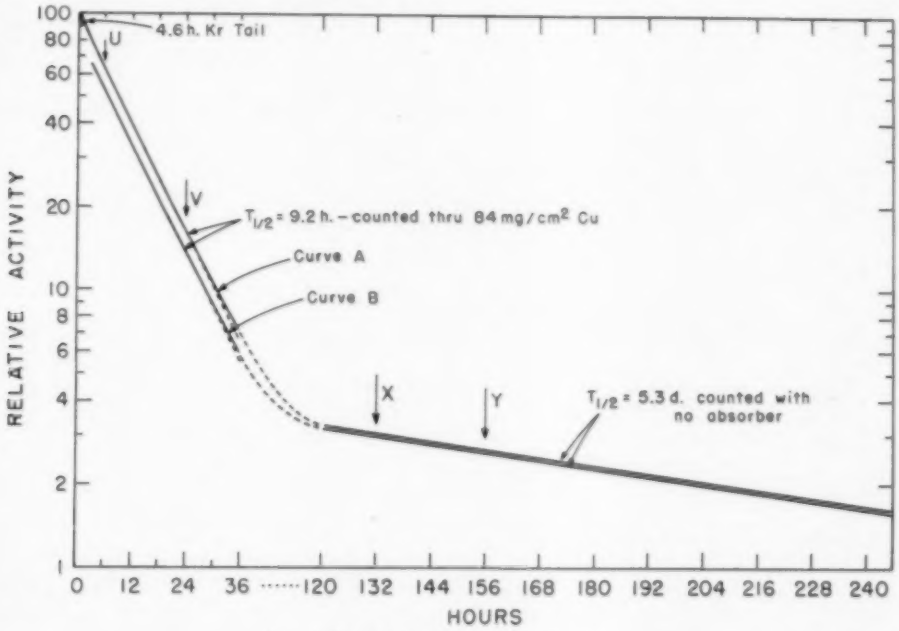

FIG. 1. Xenon decay curves (idealized).

In the second method, a single cell was filled successively with the gas samples whose activity ratio was desired; each was measured with reference to a standard of activity; decay corrections were made along a decay curve followed on a sample of the same gas in a similar cell.

A simplified outline of the procedure used in filling and counting cells appears in Table 3. Cells Nos. 7 and 8 were used in the single-cell method; cell pairs Nos. 3/4 and 5/6 in the paired-cell method. The procedure covers portion "*u–v*" of curves *A* and *B* of Fig. 1 (counted through 84 mg/cm² Cu) for the 9·2-h Xe, and portion "*x–y*" (counted without absorber) for the 5·3-day Xe. Decay corrections for the sample readings were calculated from these curves. ("No. 1 gas" means gas from quartz tube No. 1, etc.)

The cells were mounted on shelves on the air-ionization chamber, and, in the case of the 9·2-h Xe measurements, an 85-mg/cm² copper absorber on an aluminium frame was fitted to the cell. The activity was measured by a null method with the FP54 amplifier circuit. The potentiometer had been calibrated against a type K potentiometer and found accurate to 0·01%. Saturation curves of ion current had been taken on samples tenfold higher in activity, and saturation to within 0·1% per hundred volts collecting voltage was found, which gave adequate stability for this experiment. The high-resistance grid-leak was constant to 0·1% over a six-week period including the experiment, so that variations over periods of a few hours are negligible. An activity standard (Ra*DEF*) was frequently used; the measurements by the "single cell" method were referred to unit activity of this standard. Variations of about 2% in the apparent activity of such standards were observed. They were attributed largely to variation in the air density in the ion chamber with changes in atmospheric

TABLE 3.—ORDER OF CELL FILLINGS

Single cells (7 and 8)	Paired cells (3/4 and 5/6)
Fill with gases in the following order:	Fill with gases in the following order:
Master gas (unirradiated, stock gas in glass storage bulb).	Fill all with master gas (unirradiated, in glass storage bulb).
No. 3 gas (unirradiated, sealed in quartz tube).	Fill Nos. 4 and 6 with No. 3 gas (unirradiated sealed in quartz tube).
No. 1 gas (bombarded, in quartz tube).	Fill Nos. 4 and 6 with No. 1 gas (bombarded in quartz tube).
No. 2 gas (bombarded, in quartz tube).	Fill Nos. 4 and 6 with No. 2 gas (bombarded in quartz tube).
Master gas.	Fill Nos. 4 and 6 with master gas.
(Interval between sets of readings, about two hours)	

Each measurement on cells filled with "master" gas constitutes a check on the cell calibrations for 9·2-h Xe^{135} at first, and later for 5·3-day Xe^{133}.

temperature and pressure, since a correction applied to the standard readings referring to a standard temperature and pressure reduces the spread to 0·1%.

The activity measured gave about 1 volt across 10^{11} ohms, corresponding to approximately 40 microcuries of 9·2-h Xe or 20 microcuries of 5·3-day Xe per cell. The measured activities were corrected: (1) to unit standard activity; (2) for decay between successive readings for the cell pairs,

TABLE 4.—SUMMARY OF DATA

Gas sample No.	P	nv ($\times 10^{-12}$)	t	σ ($\times 10^{18}$ cm^2)
1	1·2294 ± 0·0058	1·461 ± 0·07	15 h ± 1 min	2·62 ± 0·14
2	1·2037 ± 0·0075	1·347 ± 0·07	15 h ± 1 min	2·55 ± 0·14
3	0·9984 ± 0·0022	—	—	

σ (average) = 2·58 ± 0·10 × 10^{-18} cm^2.

and, for the single cells, for decay between sets of measurements; (3) for the residual backgrounds in the cells; and, (4) for the variations in filling-temperature and pressure. Averaged values for the ratios (P) obtained are listed in Table 4, column 2, together with mean deviations.

Curve *B*, Fig. 1, illustrates the decay of a gas sample from quartz tube No. 1, beginning soon after the neutron bombardment. The diminution in the 9·2-h activity referred to curve *A*, is readily seen, and amounts to about 18%. The 5·3-day Xe^{133} tails on the curves are seen almost to superpose, indicating a very small handling effect, less than 0·5%. Larger handling effects, up to 5%, were obtained on sealing xenon activity without xenon carrier into quartz bulbs. The effect seems to be associated with the sealing-off process, since storage of xenon activity in similarly prepared quartz tubes, but using stopcocks instead of sealing off, produced a negligible handling effect over several days. This latter experiment, without carrier, indicates a probably negligible effect associated with the storage of xenon activity with carrier in glass. Thus, the handling effect observed with 5·3-day Xe^{133} several days after bombardment in the irradiated samples may be applied to the 9·2-h Xe^{135} which was measured after short storage periods.

The neutron-induced activity in the carrier xenon was estimated to contribute 0·03% to the 9·2-h Xe, based on the results of several previous xenon irradiations. The long-lived component in

activated xenon has been observed several times to have a 7-day half-life[16] instead of 5·3 days, and this activity has a softer beta component than the 5·3-day Xe^{133}, so that in our experiment it shows up to the extent of 0·1% in the measurement of the handling effect. This correction is included in Table 4.

Included in the gas mixture which was irradiated was some gas present from the dissolving, which was not easily separable from xenon. Samples of such gas from previous experiments were irradiated with neutrons. From the measured induced activity we estimate the contribution from this source to be insignificant.

It is also notable that the control sample No. 3 gave an effect in P of $0{\cdot}0016 \pm 0.0022$, which is much less than the probable error in samples Nos. 1 and 2. This furnishes an indication of the possible accuracy in determining P. The average deviations in P correspond to deviations in ln P (and in the cross-section of Xe^{135}) of 2·3% for sample No. 1 and 3·3% for example No. 2.

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Measurement of Neutron Flux

Two independent methods were used to determine the neutron flux nv to which the xenon gas was exposed; the neutron activation of gold foils to give Au^{198} activity and the neutron fission of natural uranium to produce 12·8-day Ba^{140} activity.

Gold-foil measurements. A relative activation method for the gold foils was chosen in which the neutron-flux determination is independent of the activation cross-section of gold. This was effected by comparing the activation (A_s) produced in a gold foil irradiated in a fixed position in a standard "Sigma" graphite pile, using for a source of neutrons a calibrated Ra-Be standard source, with the activation (A_H) produced by irradiating the same foil in the thimble of the heavy-water pile. The intercomparison of the latter very active foil with the low activity produced in the foil irradiated in the standard pile involves the use of a series of lead absorbers (which were intercalibrated stepwise),[17] to enable both activities to be counted on the same G-M tube. This comparison leads to a factor F relating the activity measured in a gold foil on the standardized G-M tube with one of the lead absorbers, to the known flux of the standard pile.

The very high activity produced in similar gold foils irradiated simultaneously with the xenon gas precluded their measurement on the standardized G-M tube, even through the heaviest absorber, so a further intercalibration was necessary. To this end, prior to the xenon experiment, two gold foils were irradiated in the pile thimble for one hour. These were mounted on a brass frame, and gamma activity from the Au^{198} was measured on the ionization chamber used for the xenon measurements, through a heavy glass absorber, sufficient to filter out the beta activity. The activity was followed until it had decayed enough to be counted on the standard G-M tube through the heaviest lead absorber. This count, corrected for the decay of Au^{198}, gave a calibration of the ion-chamber reading in terms of neutron flux. A repetition of this experiment gave values agreeing to within 0·3%.

A recalibration[18] of the standard-pile flux vs. the flux in the thimble of the heavy-water pile was made with gold foils by an alternate technique. A foil was irradiated in the standard pile and the gold-beta activity was measured on a G-M tube. By correcting for self-absorption in the foil, using a lead-beta absorption curve for the Au^{198} activity as a guide, the relative beta activity in the foil could be calculated. A similar foil was irradiated in the heavy-water pile thimble, and gammas from this foil were measured on the ionization chamber, from which count a flux value was calculated, as above. This foil was then dissolved and a small aliquot was mounted on platinum (to give similar backscattering to that obtaining to the standard-pile foil counting), and betas were counted on the same G-M tube. From the ratio of the beta-disintegration rates of the two samples a flux value was determined, which was $5 \pm 2\%$ higher than that found for the same foil by the method employing the ionization chamber and the series of intercalibrated absorbers. Allowing for the likelihood of cumulative errors in the absorber intercalibration and in estimating the resolving time-corrections on the G-M tube, the calibration factor based on the counting of betas from the thin (aliquot) sample appears to be more reliable and is used hereinafter.

The inaccuracy in this relative activation method includes a stated uncertainty in the calibration of the standard Ra-Be neutron source of at most $\pm 10\%$.

[16] This is now known to be due to the presence of 12-day Xe^{131} in small amounts.

[17] We are indebted to Dr. A. WATTENBERG for supplying us with these data, and to Dr. A. H. JAFFEY for rechecking the calibration.

[18] A. H. JAFFEY and L. B. MAGNUSSON *Argonne National Laboratory Report*, ANL-4030 (September 12, 1947).

A correction must be made to the flux-calibration factor to account for the difference in the resonance activation of Au^{197} produced in the standard and heavy-water piles by neutrons above the cadmium cut-off (0·25 eV). This correction was ascertained by measuring Cd ratios (K = Cd ratio = activity induced in Au foil/activity in same foil when wrapped in Cd foil). Values of K for the standard pile (K_s) of 6·1, 5·8, and 5·5, and for the heavy-water pile (K_H) of 4·4 and 4·25, were obtained. From these, one calculates

$$\frac{nv \text{ (heavy-water pile)}}{nv \text{ (standard pile)}} = \frac{K_s/(K_s - 1)}{K_H/(K_H - 1)} \times \frac{A_H}{A_s} = 0.930 \frac{A_H}{A_s} . \quad (5)$$

Thus the gold-foil-flux value times 0·930 accounts for the difference in the epicadmium activations.

A second correction to account for the difference in the effective thermal neutron temperatures obtaining in the standard pile (for which the neutron temperature is estimated to be 293°C) and the heavy-water pile (measured neutron temperature of 400°C) requires that, for a gold $1/v$ absorber, the neutron flux in heavy-water pile be corrected by a factor

$$\sqrt{\frac{T_H}{T_s}} = \sqrt{\frac{400^\circ\text{C}}{293^\circ\text{C}}} = 1.168.$$

The final correction factor applied to the gold-flux values refers to the "shadowing" effect of the two gold foils on the xenon gas in the quartz tube, which decreases the average neutron flux by 0·5%.

The gold-foil monitors on the quartz irradiation tube containing the 9·2-h Xe^{135} were measured on the ionization chamber several hours after irradiation of the xenon gas. Over a period of seven half-lives they exhibited a half-life of 64·8 ± 0·1 h. Using the calibration and correction factors described above, the flux values applicable to each end of each quartz tube were calculated (column 1, Table 5), and averaged in column 2.

TABLE 5.—NEUTRON FLUX MEASUREMENTS

	I	II	III	IV
Gas sample No.	Au foils at each end of tube	nv ($\times 10^{-12}$)		Average [(U + Au)/2]
		Au foils (average)	U monitors	
1	1·460 1·474	1·467	1·455	1·461 ± 0·07
2	1·302 1·352	1·327	1·367	1·347 ± 0·07

Fission-product measurements. The small encapsulated uranium slugs were removed from the quartz tubes, dissolved, and analysed for 12·8-day Ba^{140} activity according to a standard procedure, mounting the barium as chromate and counting in standard thin-window G-M counters. The procedure followed was that used in the determination of the absolute fission yield of 12·8-day Ba, so that such corrections as for sample and external absorption need only be applied in the same manner as in the standardizing experiment[11] to minimize, in first approximation, the errors inherent in such corrections. Corrections were applied for resolving time-losses with respect to a standard; for geometry; for chemical yield, aliquot, and weight of uranium slug; for barium decay; and for duration of bombardment.

The cross-section of natural uranium (approximately a $1/v$ absorber) for thermal neutrons having an approximately Maxwellian distribution in momentum at the mean temperature (400°C) measured

for the thermal neutrons in the heavy-water pile, was calculated from the cross-section for 2200 m/sec neutrons ($\sigma_0 = 3{\cdot}91$ barns at $T_0 = 293°C$) using the formula

$$\sigma_T = \sigma_0 \frac{\sqrt{\pi}}{2}\sqrt{\frac{T_0}{T}} = 2{\cdot}97 \text{ barns.}$$

Fast fission in U^{235} accounts for 3% of the total fission, and must be subtracted since the capture cross-section of xenon is due to thermal neutrons. The uranium monitors were located at the bottom or high flux end of the quartz tubes, so one obtains the average flux seen by the gas by multiplying the uranium-flux value by the ratio of the average of the gold-flux values to the one at the bottom. A third correction accounts for self-shadowing of the rather thick (100 mg/cm²) uranium foil, which leads to a calculated 2% increase in the average flux value. Neutron absorption in the quartz tube and vial were calculated to be negligible.

For a value of 6.32%[19] for the fission yield of 12·8-day Ba^{140}, the neutron fluxes, averaged for four analyses on each uranium foil, and including the aforementioned corrections, are as indicated in Table 5, column 3. They are seen to agree within 3% with the gold-foil values. Column 4 gives the average of gold- and uranium-monitored neutron fluxes with estimated errors.

Results

Table 4 summarizes the results of the experiment, and column 5 lists the values for the absorption cross-section (σ_c) of 9·2-h Xe^{135} for thermal (heavy-water pile) neutrons. The average value of σ_c is 2·58 megabarns $\pm$ 4%; we estimate that the error is about twice the 4% measure of precision.

CRITIQUE OF RESULTS OF Xe^{135} CROSS-SECTION MEASUREMENTS

Table 6 lists the results of the various experiments reported in this article and in other Elliott-type depletion experiments,[10, 20] their indicated errors, and the errors (estimated) in the separate factors (equation 4) from which the cross-section was calculated, together with a description of the pile and sample location in which the neutron bombardment of the 9·2-h Xe^{135} was carried out. The values of σ_c determined by measurements on the behaviour of the pile-reproduction constant are given for comparison.

The most accurate determination of the depletion ratio is that reported in experiment No. 2 of this paper. The probable error assigned is 0·5%, whereas the counting errors and systematic errors connected with counting-cell calibrations and backgrounds in all the other experiments are probably not less than 2%. In this experiment the recognized possibilities for systematic errors were all carefully checked and found to be small, and corrections for them were made. For this experiment the error in σ_c due to error in the ratio P would be 3%; for the other three Elliott-type experiments, 12% is a minimum estimate.

The comparison of neutron fluxes is on a much less precise basis. A series of experiments[21] in which comparisons were made between several methods of neutron-flux determination, including gold-foil activation and fission-product analysis, indicate

[19] L. Yaffe, H. G. Thode, W. F. Merritt, R. C. Hawkings, F. Brown, and R. M. Bartholomew *Canad. J. Chem.* **32**, 1017 (1954).

[20] A second Elliott-type experiment was carried out at Clinton Laboratory by L. A. Pardue, C. D. Moak, P. W. Levy, E. O. Wollan, and E. Meiners *Clinton Laboratory Report* CP-2600, designated III in Table 6. In this experiment the discrimination against 5·3-day Xe^{133} and other activities produced in the irradiation of the carrier gas was made by counting the 0·90 MeV betas of 9·2-h Xe^{135} in coincidence with 0·26 MeV gammas.

[21] T. B. Novey and A. H. Jaffey, private communication; T. B. Novey *Metallurgical Laboratory Report* CP-2825; A. H. Jaffey and L. B. Magnusson *Argonne National Laboratory Report* ANL-4030 (September 12, 1947).

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TABLE 6.

Experiment		Location of sample in pile	Mean neutron temperature in pile (at sample)	Estimated minimum error in σ due to error in P	Estimated minimum error in σ due to error in nvt	σ-Xe^{135} (megabarns)
"Elliott" depletion experiments	I[10]	Clinton pile pneumatic tube	520°K	±12%	±20%	1·35 ± 25%
	II	Metallurgical Laboratory heavy-water pile thimble	400°K	±12%	±12%	2·36 ± 25%
	III[20]	Clinton pile pneumatic tube	520°K	±12%	±10%	2·23 ± 16%
	IV	Metallurgical laboratory heavy-water pile thimble	400°K	±3%	±7%	2·58 ± 8%
"Pile kinetics" experiments		Hanford Pile	475°K	Fission yield of 5·9% assumed for Xe^{135}		3·3 ± 10%
		Clinton Pile[1]	380°K			2·7 ± 15%
		Heavy-water Pile[3]	400°K			1·9 ± 50%

discrepancies of 10–15% in the flux values for the same neutron source. Undoubtedly, the comparison of different fluxes in different piles is even less precise, owing to uncertainties in effective neutron temperatures, the variations from $1/v$ response of the detecting absorbers, and the deviations from Maxwellian neutron-energy distributions obtaining.

Though the agreement between the flux values of experiment No. 2 of this paper as determined by gold-foil and by fission-product activation is certainly fortuitous, the flux determination is probably more certain than in any of the other experiments; this is owing to the use of the relative gold-foil activation technique (see text) which was extensively checked by the work of T. B. NOVEY and A. H. JAFFEY of this laboratory and to the check furnished by the fission-product activation results. An estimated error of ±7% is attributed to this flux value.

For the flux determination of experiment No. 1 by fission-product analysis, an error of ±15% may be conservatively applied.

The coincidence-counting experiment[20] employed gold-foil activations for neutron-flux measurements. Data from bismuth foils also used were much less reliable. The gold-foil measurements required absolute beta-counting of the Au^{198} activity, which could not be done to better than perhaps $\pm 10\%$, what with state of development of precision-geometry standards together with absorption and scattering difficulties which were not too well ascertainable at the time of these experiments (1945).

With the exception of the first Elliott-type experiment,[10] the values are in substantial concordance, within stated limits of error. Inasmuch as the very high cross-section is due to a resonance close to the thermal region,[22] one anticipates a sensitive dependence of the measured value on the actual neutron temperature obtaining in each experiment. Thus, considering the range of neutron temperatures employed in the experiments, the results for the cross-section are in satisfactory agreement.

From the measurement of the capture cross-section of Xe^{135} as a function of neutron kinetic energy,[23] a value for the cross-section for a Maxwellian distribution in energy of neutrons at a mean temperature of 400°K (Table 6, experiments 2 and 4) may be obtained. Integration indicated a cross-section[23] of $\sim 2{\cdot}5 \times 10^{-18}$ cm², in agreement with experiments 2, 3, and 4.

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[22] S. Bernstein, M. M. Shapiro, C. P. Stanford, T. E. Stephenson, J. B. Dial, S. Freed, G. W. Parker, A. R. Brosi, G. M. Hebert, and T. W. DeWitt, *Phys. Rev.* **102**, 823 (1956).
[23] S. Bernstein, private communication.

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SZILARD-CHALMERS PROCESS FOR OSMIUM FROM HEXACHLOROOSMATE(IV) TARGETS

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(*Received* 30 *November* 1955)

Abstract—A Szilard-Chalmers concentration of Os^{191} has been achieved from targets of $(NH_4)_2OsCl_6$. Recoveries with enrichment factors greater than 10 were attained by a nitric-acid distillation separation of OsO_4 following irradiation. The separation was shown to depend upon the relative kinetics of nitric-acid oxidations.

THE measurement of the relative yield of the photonuclear process $Os^{192}(\gamma,n)Os^{191,191m}$ was undertaken. It was intended to compare this process with the photonuclear reaction of another element in a target compound with a definite, known composition. A target of ammonium hexachloroosmate(IV) was chosen in which the $Os^{191,\,191m}$ yield could be compared with the $Cl^{35}(\gamma,n)Cl^{34}$ activation. In early experiments the osmium was separated from the radioactivities of other heavy-metal elements, which were induced simultaneously, by a conventional oxidation and distillation from nitric-acid solution.[1] It was quickly evident that different fractions of the condensate osmium possessed strikingly different specific activities, and the radioactivity was concentrated in the early distillates. Because of the advantages of high specific activities which might be available from a Szilard-Chalmers process in such samples, features of the separation were investigated further.

EXPERIMENTAL

Materials and apparatus. Osmium was obtained as the tetraoxide from the Mallinckrodt Chemical Co. OsO_4 was reduced to osmium(IV) by an HCl solution of iron(II) according to the procedure of DWYER and HOGARTH.[2] $(NH_4)_2OsCl_6$ was crystallized from the reaction solution by adding NH_4Cl. Crystals were dried in a vacuum desiccator over P_2O_5.

Counting samples of osmium were prepared as circular metallic deposits with a 2·00-cm diameter by electroplating on to a 0·002-in. platinum foil. The deposits were grey, metallic, and adherent. With careful control of the electrodeposition procedure which was developed, there was no discernible clumping for thicknesses up to 12 mg/cm² when the surfaces were examined under a low-power binocular microscope. The electrodeposition was accomplished by a current of 1–2 amp passed for a period of one hour through a plating bath near the boiling temperature. The plating bath of about 20-ml volume was prepared by adding a NaOH solution of OsO_4 to 5-10 ml of a solution composed of 20 g $(NH_4)_2PO_4$, 90 g Na_2PO_4, and 5 g NaCl per 1000 ml. Additional phosphate solution was added if the solution became coloured during electrolysis. The plates were washed with H_2O and acetone and were dried at 70°C.

Counting rates of the thin electroplated osmium deposits were measured by a flow-gas, windowless Geiger-Müller counter. After 4-h irradiations, the *L*- and *M*-conversion electrons of Os^{191m} comprised the primary activity which was counted. Samples with thicknesses of 0·3 to 12 mg/cm² were prepared for the empirical evaluation of a self-scattering function, so that disintegration rates

[1] W. W. SCOTT *Standard Methods of Chemical Analysis* 5th ed., Vol. 1, Edited by N. H. FURMAN, D. Van Nostrand Co., Inc., New York, N.Y., 1939, p. 748.
[2] F. P. DWYER and J. W. HOGARTH *J. Proc. Roy. Soc. N. S. Wales* **84**, 194 (1950).

of the samples might be accurately compared by means of the technique of HOFFMAN and MARTIN.[3] The consistency of the self-scattering curve served as a very sensitive indicator of the uniformity of the deposits prepared by a given procedure. The conditions of the electroplating had to be carefully controlled; however, the procedure described produced excellent deposits. All counting rates for the 14-h component were converted to a standard sample thickness for the comparison. Each sample was followed for an extended period of decay in order to identify the 14-h component.

Separation procedure. The target compound was dissolved in a minimum amount of water after irradiation. This solution was introduced into the 300-ml round-bottom flask of a distillation apparatus. Nitric acid was added to the flask from a separatory funnel. The flask was heated by a mantle and the distillation was performed with a current of air bubbled through the solution by means of an aspirator. The distillate and air-stream were drawn through two traps, the first containing 5 ml of NaOH and the second containing 5 ml of the phosphate plating solution. A stopcock arrangement permitted the introduction of fresh traps without interruption of the distillation. The apparatus was all glass; stopcocks and standard taper joints were lubricated with water. Distillation rates of the order of 1 mg Os/min were achieved, and the amount of the distillate could be estimated from the colour of the solution in the traps. Contents of both traps were combined for electroplating of the counting samples.

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RESULTS AND DISCUSSION

Results of some separations by the distillation procedure are included in Table 1. The "enrichment factor" for a fraction was taken as the (per cent total Os^{191m} activity/per cent of total Os by weight).

For the first distillation of Table 1 the crystals of $(NH_4)_2OsCl_6$ were dissolved shortly after irradiation in the distillation flask. The HNO_3 was added, and distillation started immediately. The first few milligrams of the OsO_4 distillate carried 62% of the activity. The enrichment in this case, ca. 10, was sometimes exceeded if a smaller initial fraction were collected. The procedure therefore provides a valuable, but not especially spectacular, concentration of osmium activity for the preparation of counting samples. The recovery and the enrichment were somewhat erratic, and appeared to depend upon acid concentration and heating rate as well as the magnitude of the first fraction.

Other experiments have provided more information concerning the intermediates in the Szilard-Chalmers process. It appears that only the tetraoxide can be distilled. OsO_4 cannot be formed within the crystals of $(NH_4)_2OsCl_6$, but can appear only after the samples are placed in the aqueous solution. With one irradiation of 470 mg of $(NH_4)_2OsCl_6$, 7·5 mg of Os as OsO_4 carrier in solution was added to the freshly dissolved target compound. The OsO_4 was extracted into CCl_4, and the carrier was recovered quantitatively from the organic phase by a procedure similar to the one of GILE *et al.*[4] Only 1·3% of the activity had extracted from the organic phase, and the specific activity of the sample was less than 40% that in the aqueous phase. A subsequent distillation provided the typical substantial concentration of activity. Therefore, OsO_4 is not formed immediately when the crystals dissolve, but some other chemical species must arise. The separation therefore depends upon the relative kinetics of oxidation of the intermediate species and the $OsCl_6^{=}$ ion. In several experiments the specific activity of later distillates fell significantly below the value for the still residues. Such a result requires that some of the Os^{191m} atoms must form additional species which are oxidized more slowly than $OsCl_6^{=}$. Therefore, the

[3] D. C. HOFFMAN and D. S. MARTIN JR. *J. Phys. Chem.* **56**, 1097 (1952).
[4] J. D. GILE, W. M. GARRISON, and J. G. HAMILTON, U.S. Atomic Energy Commission Report No. UCRL-804 (1950).

TABLE 1.—Os^{191m} RADIOACTIVITY IN FRACTIONS RECOVERED FROM IRRADIATED HEXACHLOROOSMATES(IV)

Target	Fractionation	Fraction wt. (mg Os)	Counting sample wt. (mg Os)	Per cent recovered activity	Enrichment factor
$(NH_4)_2OsCl_6$	Add 10 ml conc. HNO_3 Distil, Condensate No.				
	1	5·1	2·7	62	9·9
	2	7·8	7·0	6	0·6
	3	12·3	11·1	7	0·5
	4	4·2	3·8	2	0·4
	5	3·2	2·9	2	0·5
	6	6·5	5·8	2	0·3
	Still residue	42·0	3·2	19	0·4
	Total	81·0			
$(NH_4)_2OsCl_6$	Add 20 ml H_2O, distil, Condensate No. 1	5·7	2·4	7	2·2
	Add 10 ml 0·20M HNO_3, Condensate No.				
	2	15·9	5·6	25	2·9
	3	5·4	2·7	8	2·7
	4	2·7	2·1	4	2·7
	Add 5 ml 2·0M HNO_3, Condensate No 5	6·3	4·0	10	2·9
	Still residue	146·6	7·3	56	0·7
	Total	183			
K_2OsCl_6	Add 5 ml conc. HNO_3 distil, condensate No.				
	1	0·5	3·3[a]	8	6
	2	1·1	3·8	5	1·7
	3	0·9	2·7	0·4	0·2
	Still residue	34·0	3·4	87	0·9
	Total	36·5			

[a] Carrier added to this group for plating.

activity not collected in the initial enriched fraction does not completely represent retention in the form of the target compound. Co-ordination complexes of Os^{III}, Os^{IV} are, in general, exceedingly inert toward substitution reactions; e.g. exchange between Cl^- and $OsCl_6^=$ is undetectable in two months.[5] It is reasonable, therefore, that the radioactive atoms can exist as one or more species which do not exchange with the $OsCl_6^=$ ions.

In the second experiment of Table 1, the neutral solution of the target salt was heated in the distilling flask. The formation of a green solution indicated the probable formation of $[OsCl_5(OH)]^=$.[2] A distillate of 5·7 mg Os was collected from the air-stream; however, the enrichment was very low. Again, the experiment indicated that the radioactivity did not exist as OsO_4 before the addition of nitric acid. After the addition of limited amounts of dilute HNO_3, subsequent distillations gave only moderate enrichments. It appeared that the Os^{191m} existed in a form whose oxidation by nitric acid was of higher order in nitric acid than the oxidation of the principal target complex.

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An interesting observation was made when potassium hexachloroosmate(IV) target was substituted for the ammonium salt. The rate of oxidation of the osmium was at least an order of magnitude lower. Although very small distillate fractions were collected, the enrichment, within the rather low accuracy for the experiment, was very poor. Hence, in the oxidation process the ammonium ion has an important role in providing a fairly rapid oxidation of the osmium and in the enrichment for the Szilard-Chalmers process.

CHRISTIAN, MITCHELL, and MARTIN[6] and HALDAR[7] have studied Szilard-Chalmers processes for crystalline platinum co-ordination complexes. Following the recoil in the nuclear reaction, the activated atoms remained in the crystal in a state such that a number of different complex species were formed upon dissolution. With the formation of a number of inert species, a Szilard-Chalmers recovery may be poor unless a carrier for all the dominant species is added and separated. It appears that the hexachloroosmates(IV) must also yield a number of species in the solution. The concentration of the activity by virtue of the divergent oxidation kinetics must involve a complex reaction, in view of the effect of ammonium ion. The enrichment attained seems surprisingly high for a system of primarily inert-type complexes.

Acknowledgements—We wish to thank Dr. D. J. ZAFFARANO and members of the synchrotron group for their assistance and efforts in providing the irradiations.

[5] L. L. LARSON and C. S. GARNER *J. Amer. Chem. Soc.* **76**, 2180 (1954).
[6] D. CHRISTIAN, R. F. MITCHELL, and D. S. MARTIN JR. *Phys. Rev.* **86**, 946 (1952).
[7] B. C. HALDAR *J. Amer. Chem. Soc.* **76**, 4229 (1954).

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SOME IONIZATION POTENTIAL VARIATIONS AND RELATIONSHIPS

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(*Received* 10 *December* 1955)

Abstract—Ionization potential variations and relationships are considered in three parts. The first is devoted to an examination of variation of successive ionization potentials involving valence electrons in several elements. With the exception of some Group II elements in particular, the relationship

$$I_n = KZ$$

is quite closely approximated in several elements and holds both for *s* and *p* electrons, but distinctly not for *d* electrons (I_n = *n*th ionization potential; that is, the first ionization potential when Z, the ionic charge = 1, the second when $Z = 2$, etc.; K is a constant). I_n is elevated (i) when passing from *p* to *s* electrons in nontransitional elements and (ii) when passing from *s* to *d* electrons in transitional elements. The magnitude of Δ_I (the difference between two successive ionization potentials) can usually be correlated with the existence of closed shells, subshells, and valence states in general, and may serve as a useful semi-quantitative guide in this respect, provided some allowance is made for properties such as weight and size.

Variation of I_n in isoelectronic sequences is considered in the second part; the relationship[1]

$$I_n = aZ^2 + bZ$$

is closely obeyed in several sequences. For *s* electron sequences, constant a varies from R (= 13·59) in the point-charge sequence $H^+ \rightarrow N^{7+}$ to ~0·90 in some 5*s* sequences; b varies from 2·2 ($Li^+ \rightarrow F^{7+}$) to 10·9 ($He^+ \rightarrow N^{6+}$). a remains uniform at 3·5 in a series of 2*p* sequences ($B^+ \rightarrow Na^{7+} \ldots Ne^+ \rightarrow Si^{5+}$), whereas b increases from 5·4 to 16·6.

The relationship of a third variable, ionic radius (r), to I and Z is considered in the third part. r varies smoothly with both I and Z in isoelectronic sequences. Various other regularities may be observed; some involve entry of 3*d* and 4*f* electrons. For the sequence $Na^+ \rightarrow Cl^{7+}$ and for Na^+—K^+—Rb^+—Cs^+, and Mg^{2+}—Ca^{2+}—Sr^{2+}—Ba^{2+}, the relationship

$$I_n \sqrt{r} = 5Z^{1.27}$$

holds fairly well. The quantity $5Z^{1.27}/I_n\sqrt{r}$, which equals unity ± a couple of per cent for the above cations, has been suggested as a comparative measure of the shielding (screening) efficiency of cations.

INTRODUCTION

PREVIOUS papers on ionization potentials by this writer,[2, 3, 4] include brief discussions on the variation of successive ionization potentials in some elements and the relationship between ionization potential (I), ionic radius (r), and ionic charge (Z). The present paper attempts a fuller description of some of these aspects. A principal aim is to seek and demonstrate various regularities and, accordingly, emphasis will be on graphical presentation. The paper is divided into three parts. The first is concerned mainly with variation of successive ionization potentials in several elements and the

[1] E. LISITZIN *Soc. Sci. Fen., Com. Phys.—Math.* x *No.* 4 (1938)
[2] L. H. AHRENS *Geochimica et Cosmochimica Acta* **2**, 155 (1952)
[3] L. H. AHRENS *ibid.* **3**, 1 (1953)
[4] L. H. AHRENS *Nature* **74**, 644 (1954)

extent to which successive ionization potential *differences* may be correlated with shells, subshells, and the characteristic valence states of the elements. Part II is devoted to an examination of the variation of ionization potential/charge in several isoelectronic sequences, and in the final section (Part III) the relationship between ionization potential, ionic radius, and ionic charge is examined.

Ionization potentials (in volts) are from LANDOLT-BÖRNSTEIN,[5] unless otherwise stated. The manuscript had been written and the diagrams completed before attention was drawn to the more recent set of ionization potentials given by FINKELNBURG and HUMBACH;[6] for the most part, their values accord closely with those given here, but occasionally disagreement is serious, and in such cases reference may be made to both values. Ionic radii are from AHRENS,[7] most of the values in that paper being based on those of PAULING[8] and AHRENS.[2]

PART I

VARIATION OF SUCCESSIVE IONIZATION POTENTIALS IN SOME ELEMENTS

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We shall examine the Group IV elements first. Fig. 1 serves to show variations of I with Z up to $Z = 5$. Consider the first and second ionization potentials. The observation has been made[3] that the first ionization potentials of most Group IV elements are either equal or very nearly equal to one-half their second ionization potentials, and Fig. 1 shows that a line through the first two points for each of the Group IV elements usually passes close to the origin. Table 1 compares I_1 and $I_2/2$ for each of the Group IV elements. With the exception of carbon, I_1 and $I_2/2$ are very similar; that is, to within $\Delta = < \pm 0{\cdot}13$ ($< \pm 1{\cdot}5\%$). The first two ionization potentials involve p electrons in C, Si, Ge, Sn, and Pb, and s electrons in Ti and Zr. As we pass to higher ionization potentials involving different electrons (p to s in C, Si, Ge, Sn, and Pb, and s to d in Ti and Zr), a distinct step is encountered; this we shall discuss later when examining ionization potential relationships involving unlike electrons, but we may now note that extrapolation of a line passing through the third and fourth points in C, Si, Ge, Sn, and Pb (s electrons) invariably passes close to the origin. Table 1 also compares $I_3/3$ and $I_4/4$ in these elements; and in each, agreement is close—that is, to within $\Delta = < 0{\cdot}15$ ($< \sim 1{\cdot}15\%$)—and may be of either sign. Similar agreement for s electrons is found in Group III elements B, Al, Ga, In, and Tl, where $I_2/2$ and $I_3/3$ are very similar, and in Sc, Y, and La, where I_1 and $I_2/2$ are very similar (Table 2 and Fig. 2.). For higher-group elements (phosphorus, sulphur, and chlorine, for example) Δ remains very small for the pairs of s electrons; see, for example, Fig. 3. For a lone pair of s electrons outside a closed shell, Δ increases; in Be, Mg, Ca, Sr, and Ba it is still fairly small ($\Delta = \sim 2{\cdot}3\%$) but is much higher in the 18-electron elements Zn, Cd, and Hg, reaching a maximum of $+ 1{\cdot}04$ V in Hg. For details see Table 3.

We may now compare ionization potential changes involving unlike electrons; p to s in nontransitional elements and s to d in some transitional elements. Consider germanium. I_1 and $I_2/2$ (p electrons) are 8·13 and 8·00 V respectively (av. 8·07 V),

[5] LANDOLT-BÖRNSTEIN *Atom und Molekularphysik* (*I Teil*), Atom und Ionen, see p. 211. Springer (Berlin-Göttingen) 1950

[6] W. FINKELNBURG and W. HUMBACH *Naturwissenschaften* **42**, 35 (1955)

[7] L. H. AHRENS Unpublished class notes, Oxford (1955)

[8] L. PAULING *The Nature of the Chemical Bond* (*2nd ed*). Cornell University Press, Ithaca. 450 pp. (1946)

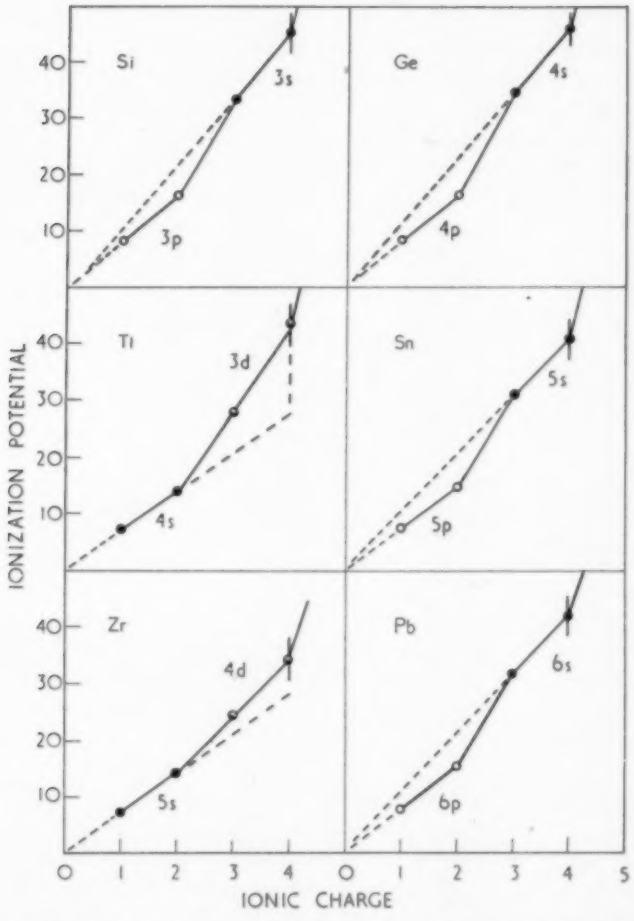

FIG. 1.—Successive ionization potentials in some Group IV elements. Extrapolated lines joining components of pairs of s and p electrons pass close to the origin, whereas those involving d electrons (Ti and Zr) pass close to I_2 (s electron) and finally intersect the Z axis.

and $I_3/3$ and $I_4/4$ (s electrons) are 11·40 and 11·45 V respectively (av. 11·43 V). In which case $I_s/I_p = 11{\cdot}43/8{\cdot}07 = 1{\cdot}42$. Similar values (Table 4) are found in several Group IV elements. This I_s, I_p comparison in Group IV seems to be quite satisfactory, as Δ is very small both for p and s electrons. In other elements containing both p and s electrons, Δ is invariably small for s electrons (see above), but the relationship between I_n and Z may not be particularly smooth for fairly large numbers (three or more) of p electrons (see P, S, and Cl—Fig. 3). Nevertheless, despite some displacement of individual points, extrapolation of a line of best fit passes quite close to the origin. In which case, the I_s, I_p relationship may be examined further, and Table 4 lists values of I_s/I_p for Group III elements, and some Group V, VI, and VII elements, in addition to those of Group IV. Inspection of Table 4 shows that the value of I_s/I_p evidently depends on the number of electrons outside a closed shell, and this relationship is shown in Fig. 4; the regularity is quite well developed. If values read off the

TABLE 1.—IONIZATION POTENTIAL-CHARGE RATIOS AND DIFFERENCES IN THE GROUP IV ELEMENTS

	I_1	$\frac{I_2}{2}$	Δ	$\frac{I_3}{3}$	$\frac{I_4}{4}$	Δ
C	11·27	12·40	−1·13	15·97	16·1	−0·13
Si	8·15	8·20	−0·05	11·17	11·30	−0·13
Ti	6·84	6·80	+0·04	(13·8	10·9	+2·9)*
Ge	8·13	8·00	+0·13	11·40	11·45	−0·05
Zr	6·94	7·00	+0·06			
Sn	7·30	7·30	0·00	10·23	10·18 (9·9)†	+0·05
Pb	7·42	7·50	−0·08	10·63	10·52	+0·11

* *d* electrons
† Another value of I_4

TABLE 2.—IONIZATION POTENTIAL-CHARGE RATIOS AND DIFFERENCES IN THE GROUP III ELEMENTS

(a) *Nontransitional elements*

	$\frac{I_2}{2}$	$\frac{I_3}{3}$	Δ
B	12·55	12·63	−0·10
Al	9·40	9·50	−0·10
Ga	10·25	10·20	+0·05
In	9·45	9·20	+0·15
Tl	10·15	9·93	+0·22

(b) *Transitional elements*

	I_1	$\frac{I_2}{2}$	Δ
Sc	6·7	6·4	+0·3
Y	6·5	6·15	+0·35
La	5·6	5·7	−0·10

curve of best fit are related to $1/N$ (N = number of electrons outside the shell), an approximately linear relationship is found (Fig. 5), the expression for which is

$$\frac{I_s}{I_p} = \frac{2{\cdot}3}{N} + 0{\cdot}83 \qquad (1)$$

For the Group IV elements Si, Ge, Sn, and Pb, use may be made of this relationship to calculate approximately any of the first four ionization potentials, provided only one is known. For example, the first ionization potentials (p electrons) of Si, Ge, and Pb ($N = 4$) are 8·15, 8·13, and 7·42 V respectively, and their respective fourth ionization potentials (s electrons) calculate as 45·8 (45·2), 45·7 (45·7), and 41·7 (42·1) V, and

agree fairly closely with measured values (Table 6) which are given in parentheses. Distinctly different fourth ionization potentials of tin have appeared in the literature, namely, 40·72,[9] 39·4,[5] and 46·4.[6] Estimates based on the first (7·3 V),

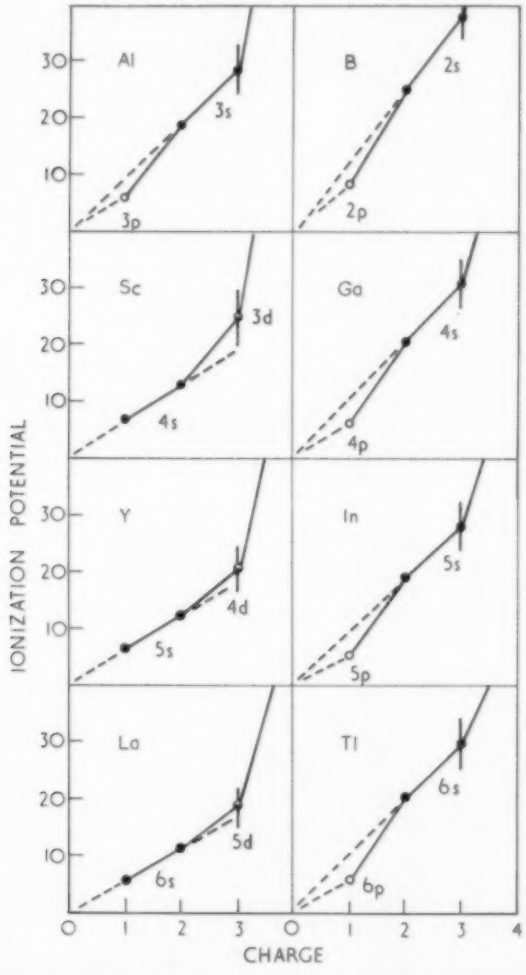

FIG. 2.—Successive ionization potentials in some Group III elements.

second(14·6 V), and third (30·69 V) ionization potentials give values of 41·03, 41·03, and 40·92 respectively, thereby supporting the value listed by HERZBERG. For C, and Group III, V, and VII elements, such calculations are very approximate.

Variation of ionization potential when passing from an *s* to a *d* electron is distinctly different from that when passing from *p* to *s*. There is again an elevation of ionization potential (Sc, Y, and La—Fig. 2), but the second *d* electron (Ti and Zr) is located close to an upward extrapolation of a line joining the second point (the second *s* electron)

[9] G. HERZBERG *Atomic Spectra and Atomic Structure* p. 201. Dover Publications, New York. 257pp. (1944)

and the third point (the first *d* electron)—see Ti and Zr in Figs. 1 and 6. Downward extrapolation of this line does not pass close to the origin, but intercepts the *Z* axis at ~1·1 for Ti and ~0·6 for Zr. Such behaviour is apparently characteristic of all

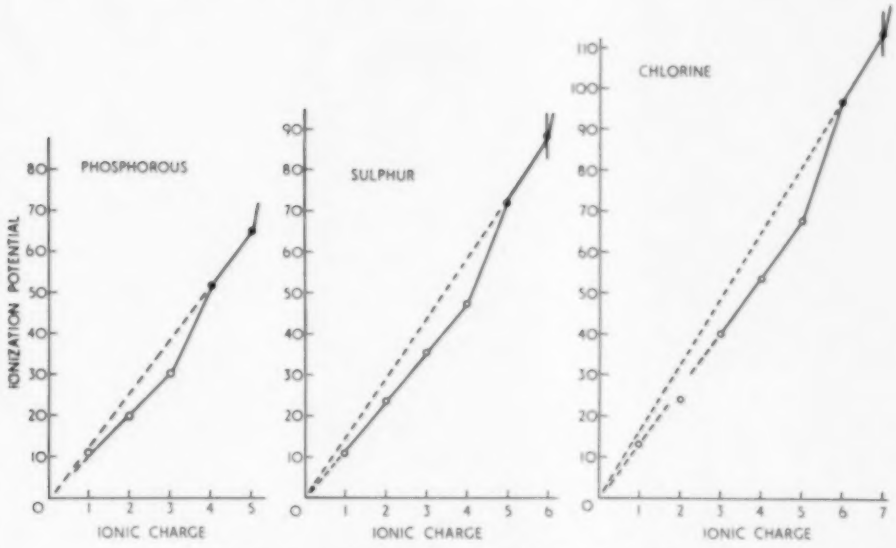

FIG. 3.—Successive ionization potentials in P, S, and Cl.

TABLE 3.—A COMPARISON OF I_1 AND $I_2/2$ IN GROUP II ELEMENTS

	I_1	$\frac{I_2}{2}$	Δ
He	24·56	27·05	−2·49
Be	9·32	9·1	+0·22
Mg	7·64	7·5	+0·14
Ca	6·1	5·95	+0·15
Sr	5·69	5·5	+0·19
Ba	5·21	5·0	+0·21
Zn	9·39	9·0	+0·39
Cd	8·99	8·45	+0·54
Hg	10·44	9·4	+1·04

I vs. *Z* relationships involving *s* and *d* electrons. Unlike the I_p, I_s relationship, which appears to be dependent on the number of electrons (N) outside a closed shell (Figs. 4 and 5), but seems to be quite independent of quantum assignment, the I_s, I_d relationship appears to depend both on N and quantum assignment. This may be seen from Table 5. If we compare the pairs Sc—Ti (4*s* and 3*d*) and Y—Zr (5*s* and 4*d*) first, we note that elevation of ionization potential (the last column) increases from 5·0 in Sc to 7·2 in

TABLE 4.—VALUES OF RATIO I_s/I_p

Electrons	Group III	Group IV	Group V	Group VI	Group VII
2*s* and 2*p*	B 1·52				
3*s* and 3*p*	Al 1·57	Si 1·4	P 1·3	S 1·21	Cl 1·16
4*s* and 4*p*	Ga 1·7	Ge 1·42	As 1·3		
5*s* and 5*p*	In 1·6	Sn 1·42	Sb 1·35	Te 1·2–1·3	
6*s* and 6*p*	Tl 1·6	Pb 1·41	Bi 1·3		
Average	1·6	1·42	1·31	1·25	1·16

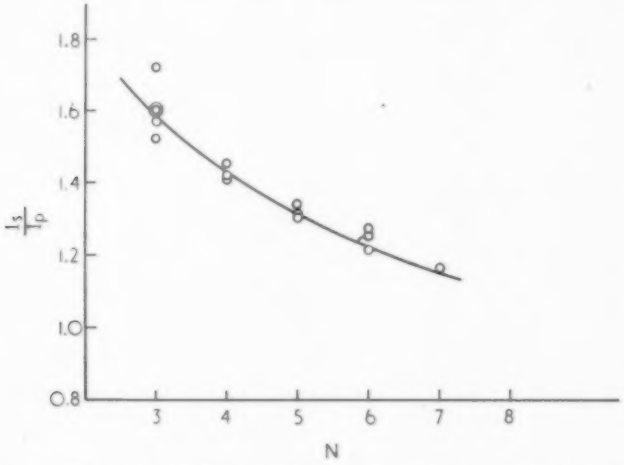

FIG. 4.—The relationship between the ratio of ionization potential per unit charge for *s* electrons to that for *p* electrons and the number of electrons outside a closed shell.

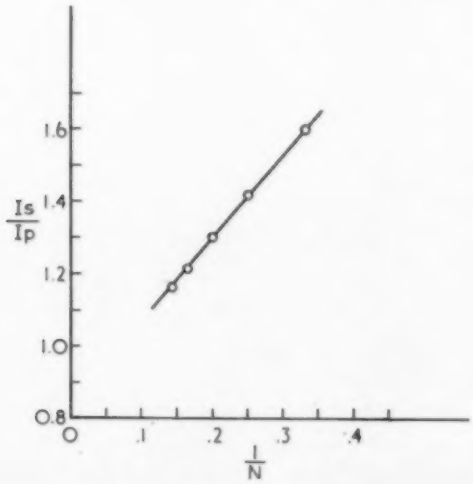

FIG. 5.—As in Fig. 4, but with 1/*N* as abscissa.

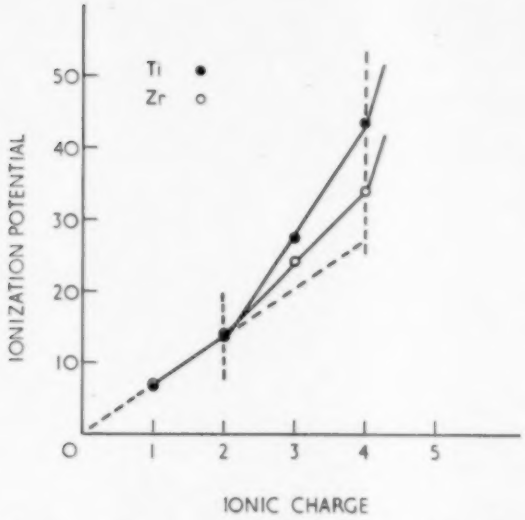

FIG. 6.—Critical comparison of successive ionization potentials in Ti (4*s* and 3*d* electrons) with those in Zr (5*s* and 4*d* electrons).

TABLE 5.—A COMPARISON OF $3I_2/2$ AND I_3 IN SOME TRANSITIONAL ELEMENTS

	$I_2 \times \frac{3}{2}$	I_3	$I_3 - \frac{3I_2}{2}$
Sc (4*s* 3*d*)	19·2	24·2	5·0
Y (5*s* 4*d*)	18·45	20·4	1·95
La (6*s* 5*d*)	17·1	19·1	2·00
Ti (4*s* 3*d*)	20·4	27·6	7·2
Zr (5*s* 4*d*)	21·0	24·1	3·1

Ti, and from 1·95 in Y to 3·1 in Zr. The significance of quantum assignment is indicated by comparing ionization potential elevation in Sc (5 V) with that in Y and La (1·95 and 2·00 V, respectively) and Ti (7·2 V) with Zr (3·1 V). The difference between 4*s* and 3*d* (Sc and Ti) electrons is evidently much greater than between 5*s* and 4*d* (Y and Zr), and 6*s* and 5*d* (La). These relationships are quite clearly evident in Figs. 1 and 2, and particularly in Fig. 6, which critically compares Ti and Zr.

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TABLE 6.—IONIZATION POTENTIALS OF GROUP IV ELEMENTS

	I_1	I_2	I_3	I_4	I_5
C	11·27	24·8	47·9	64·5	392·0
Si	8·15	16·4	33·5	45·2	165·9
Ti	6·84	13.6	27·6	43·3	99·4
Ge	8·13	16·0	34·2	45·7	93·5
Zr	6·94	14·0	24·1	34·0	<83
Sn	7·3	14·6	30·7	39·4 (41·0) (46·4)	80·9
Ce	6·54	12·30	19·5	36·5	~70
Pb	7·42	15·0	31·9	42·1	69·4
Th	*	*	*	29·4	?

* Probably all low, i.e. <8 V.

SOME OBSERVATIONS ON IONIZATION POTENTIAL DIFFERENCES AND STABLE VALENCE STATES

It has been known for some time that ionization potentials may be used as measured indications of the existence of stable shells. For example, the first ionization potential of lithium is 5·4 V and the second 75·7 V, and the electron from the K shell is apparently so tightly held that it is not available for chemical combination. As we proceed from Li to Cs, however, the second ionization potential drops progressively down to 23·4 V for Cs, and this value may perhaps be quite close to some *upper* threshold value below which the electron would be available for valence purposes. But if the second electron could be made available for such purposes, it would not necessarily follow that a divalent state would be stable, because "oxidation" to higher states might take place immediately: this possibility may depend on some *lower* threshold limit. Accordingly, an attempt will be made here to explore briefly the extent to which ionization potentials may be correlated with known characteristic valence states of several elements. AHRENS[3] has drawn attention to some correlation between the magnitude of $\Delta_{n,m}$ (the difference between two successive ionization potentials n and m) and the existence of stable valence states in some Group IV and Group V elements, and these elements will be considered first. Table 6 gives the first five ionization potentials of Group IV elements and Table 7 values of $\Delta_{n,m}$: Tables 8 and 9 give equivalent data for the Group V elements.

We may note first that $\Delta_{4,5}$ and $\Delta_{5,6}$ for Group IV and Group V elements is always large: that is, >27·3 V (lead), and these data taken together with others ($\Delta_{1,2}$ for Cs, for example) indicate a magnitude of 20–30 V as near the lower limit of the upper threshold value (Δ_{max}), which indicates a truly stable shell. We shall see, however, that properties such as weight, and perhaps size, are apparently important, and in some of the comparisons which follow cognizance will be taken of this.

Examination of Figs. 1 and 2 has shown a rise in ionization potentials in each I vs. Z plot when passing from the second to third ionization potentials. For Si, Ge, Sn, and Pb, the increase is due to the transition from p to s electrons and for Ti, Zr, Hf,

TABLE 7.—IONIZATION POTENTIAL DIFFERENCES IN GROUP IV ELEMENTS

	$\Delta_{0,1}$	$\Delta_{1,2}$	$\Delta_{2,3}$	$\Delta_{3,4}$	$\Delta_{4,5}$
C	11·27	13·43	23·1	16·1	327·5
Si	8·15	8·25	17·1	11·7	120·77
Ti	6·84	6·76	14·0	15·7	56·1
Ge	8·13	7·87	18·2	11·5	47·8
Zr	6·95	7·05	10·1	9·9	~49
Sn	7·30	7·30	16·1	8·7	41·5
Ce	6·54	5·76	7·2	17·0	~53
Pb	7·42	7·58	16·9	10·2	27·3
Th	<~8	<~8	<~8	<~8	<~35·6

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TABLE 8.—IONIZATION POTENTIALS OF GROUP V ELEMENTS

	I_1	I_2	I_3	I_4	I_5	I_6
N	14·55	29·6	47·4	77·4	97·9	551·9
P	10·9	19·7	30·2 26·5	51·4	65·0	~223
V	6·71	41·1	(29?)	~48	64·9	128·3
As	10·5	~20	28·3	50·1	62·6	127·6
Nb	<8	~13	~25	~38	~50	~106
Sb	8·64	~17	24·9	44·2	55·7	107·7
Ta	Probably less than 8–9		~22	~33	~45	?
Bi	~3·8	~17	26·6	~45	55·7	88

TABLE 9.—IONIZATION POTENTIAL DIFFERENCES IN GROUP ELEMENTS

	$\Delta_{0,1}$	$\Delta_{1,2}$	$\Delta_{2,3}$	$\Delta_{3,4}$	$\Delta_{4,5}$	$\Delta_{5,6}$
N	14·55	15·05	17·8	30·0	20·5	454·0
P	10·9	8·8	10·5	21·2	13·6	~158
V	6·71	7·39	12·4	~21·5	~16·9	63·4
As	10·5	~9·5	~ 8·3	21·8	12·5	65·0
Nb	<8	<~5	~12	~13	~12	~106
Sb	8·64	~8·36	~7·9	~19·3	~11·5	52·0
Ta	<8–9	<8–9	?	~11	~12	?
Bi	~8·8	~8·2	~9·6	~18·4	~10·9	32·3
Pa	No data available					?

and Th (not shown, as data approximate) from *s* to *d*. Si, Ge, Sn, Pb, and Ti can be divalent and in each, $\Delta_{2,3} = 14$–18 V; divalence in Zr, Hf, and Th is, however, either very feeble or unknown and, for them, $\Delta_{2,3} = <\sim 10$ V. We may note also that $\Delta_{1,2}$ is always <10–11 V (no monovalence known) and that $\Delta_{3,4}$ is $<\sim 10$–11 V in those elements in which trivalence is unknown. In those which can be distinctly trivalent (Ti and Ce), $\Delta_{3,4}$ is $>15{\cdot}7$ V. Evidently $\Delta_I = \sim 10$–11 V represents an approximate threshold lower limit which, if not exceeded, leads to immediate "oxidation" to some higher state. Correlation between Δ_I values and the existence of stable valence states and stable shells appears to hold fairly generally, and we enquire now as to whether Δ_I can be correlated with relative stabilities of *known* valence states, and for this purpose comparisons will rarely be made between elements with extremely different weights. In the pair Si and Ge, $\Delta_{2,3} = 17{\cdot}1$ and $18{\cdot}2$ V, respectively, and whereas divalence in Si is feeble, it is well developed in Ge. The pair Sn: Ti make an interesting comparison. $\Delta_{2,3}$ is low in Ti (14 V) and Ti^{II} is feebly stable; for Sn, $\Delta_{2,3}$ is $16{\cdot}1$ V and Sn^{II} is quite moderately stable. $\Delta_{3,4}$ is $15{\cdot}7$ V in Ti and Ti^{III} is stable. Zr and Th contrast sharply with Ti, and this is evidently due to the fact that the 3*d* electron is much more tightly bound than the 4*d*, and 6*d* electrons when compared with equivalent *s* electrons (Table 7, and particularly Fig. 6). Consequently, as Δ_I is not significantly elevated when passing from *s* to 4*d*, and 6*d* electrons, "oxidation" tends to proceed immediately to the quadrivalent state. In the pair Ce: Pb, $\Delta_{3,4}$ and $\Delta_{2,3}$ are quite high ($\sim 16{\cdot}8$ and $\sim 16{\cdot}9$ V respectively), and of about equal magnitude, and Ce^{III} and Pb^{II} are very stable valence states.

Similar generalizations about the existence of shells, valence states, and the stabilities of valence states usually hold also for the Group V elements. Ionization potential correlations for V—Nb—Ta are particularly interesting, but definite conclusions are sometimes not possible, as several of the higher ionization potentials are only approximately known. In the Group III elements, Al, Ga, In, and Tl, only monovalent and trivalent states are indicated. For Al, a fairly light element, $\Delta_{1,2}$ is apparently just below the threshold and no Al^{I} compounds would seem to be known. Greatest monovalent stability is shown by Tl ($\Delta_{1,2} = 14{\cdot}2$ V). However, $\Delta_{1,2}$ is slightly greater in Ga, and even if some allowance is made for weight, it seems surprising that Ga^{I} compounds are not found. It is surprising also that Ga^{II} compounds apparently exist ($\Delta_{2,3} = 10{\cdot}2$ V), but there is the possibility that such compounds are in fact Ga^{I}-Ga^{III} mixtures, which might to some extent explain these apparent anomalies. In the group Sc, Y, and La, only trivalent states are known, although, for Sc, $\Delta_{2,3} = 12{\cdot}0$ V, which is probably not very far below the threshold; in the elements which immediately succeed Sc, namely Ti, V, etc., the threshold is exceeded, and divalent as well as higher states exist.

When used as a measured indication of the existence of shells and also possible valence states and their stabilities, it seems that the magnitude of Δ_I generally decreases with weight.

PART II

IONIZATION POTENTIAL VARIATIONS IN SOME ISOELECTRONIC SEQUENCES

LISITZIN[1] has discussed change of ionization potential in certain isoelectronic sequences, and gives a full bibliography. In several sequences, particularly those

involving the lighter elements, the relationship between ionization potential and ionic charge is fairly simple, and may, to a good first approximation, be expressed by an equation of the type

$$I_n = aZ^2 + bZ \qquad (2)$$

where a and b are constants and Z ionic charge. In the plots which follow (Figs. 7–10) I_n/Z is related to Z. For s electrons (Figs. 8, 9, 10) the upper abscissal scale is for sequences involving the first s electron outside a closed shell ($H^+ \rightarrow N^{7+}$, $Li^+ \rightarrow F^{7+}$, for example), whereas the lower scale, displaced by one unit, is for sequences involving the second s electron ($He^+ \rightarrow N^{6+}$, $Be^+ \rightarrow F^{6+}$, for example). Graphs involving s electrons have been drawn this way, so that careful comparison may be made of I_n/Z for pairs of s electrons; for example, Be (I_1/I and $I_2/2$), B($I_2/2$ and $I_3/3$), and so on.

Values of constants a and b (equation 2) for each sequence with fairly well developed linearity are given in Table 10. Some values of $a^{(1)}$ are given for comparison.

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TABLE 10.—VALUES OF CONSTANTS a AND b

Electron	Sequence	a		b	Fig.
		LISITZIN	(This paper)		
1s	$H^+ \rightarrow N^{7+}$ (point charges)	—	13·59	—	7
1s	$He^+ \rightarrow N^{6+}$	13·54	13·59	10·9	7
2s	$Li^+ \rightarrow F^{7+}$	3·41	3·43	2·2	8
2s	$Be^+ \rightarrow F^{6+}$	3·44	3·43	5·6	8
3s	$Na^+ \rightarrow Ca^{10+}$	1·62	1·72	4·4	9
3s	$Mg^+ \rightarrow Ca^{9+}$	—	1·72	6·1	9
4s	$Cu^+ \rightarrow Kr^{8+}$	1·12	1·17	6·6	Part of Fig. 11
4s	$Zn^+ \rightarrow As^{4+}$	—	1·17	7·8	Part of Fig. 11
5s	$Ag^+ \rightarrow I^{7+}$	0·91	~0·90	~6·6	Part of Fig. 12
5s	$Cd^+ \rightarrow I^{6+}$	0·94	~0·90	~7·6	Part of Fig. 12
6s	$Au^+ \rightarrow Po^{6+}$	0·87	see text		
2p	$B^+ \rightarrow Na^{7+}$		3·5	5·4	Fig. 10
2p	$C^+ \rightarrow Ne^{8+}$		3·5	7·8	Fig. 10
2p	$N^+ \rightarrow Mg^{6+}$		3·5	10·0	Fig. 10
2p	$O^+ \rightarrow Si^{7+}$		3·5	10·6	Fig. 10
2p	$F^+ \rightarrow Al^{8+}$		~3·5	13·6	Fig. 10
2p	$Ne^+ \rightarrow Si^{8+}$		~3·4	16·6	Fig. 10
3d	$Sc^{9+} \rightarrow Fe^{8+}$		~2·0	4·3	Not shown

It is known that for point charges ($H^+ \rightarrow F^{7+}$), $I_n = aZ^2$ where $a = R$, the Rydberg constant which is equal to the first ionization potential of hydrogen. In the 1s sequence, $He^+ \rightarrow N^{6+}$, constant a remains the same ($=R$) and $b = 10{\cdot}9$ V; that is, it is about

equal to the difference between the first ionization potentials of He and H (24·56 — 13·59 = 10·97 V). This difference is hereafter indicated by R'. For $2s$ isoelectronic sequences $a = \sim R/4$, and b roughly $R'/5$ and $R'/2$. In the $3s$ sequences, a reduces to half the value of a for the $2s$ sequences and thus equals $R/8$. a reduces to 1·15 in the $4s$ sequences; that is, to two-thirds of 1·7 ($3s$ sequence), and it approximately equals $R/12$. For the $5s$ sequences, the reduction is to 0·9 V. For the $6s$ sequence starting with Au^+, the relationship between I_n/Z and Z shows much curvature, and equation (2) cannot be made to apply. The variation of a in the $2s$, $3s$, and $4s$ sequences seems to follow roughly the relationship

$$a = \frac{R}{4n} = \frac{3{\cdot}4}{n}$$

where $n = 1$, 2, and 3 for the $2s$, $3s$, and $4s$ sequences respectively. For sequences involving the first of a pair of s electrons, constant b appears to vary regularly in steps

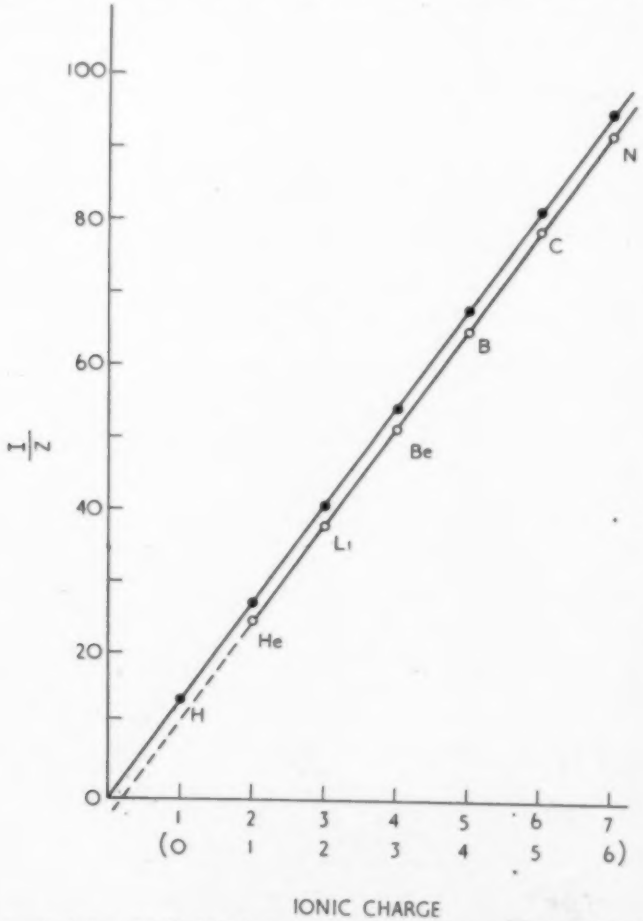

FIG. 7.—Variation of I_n/Z with Z in the ls isoelectronic sequences $H^+ \rightarrow N^{7+}$ (point charges–full circles) and $He^+ \rightarrow N^{6+}$, open circles. The abscissal scale for the $He^+ \rightarrow N^{6+}$ sequence is displaced by one unit, as indicated (lower scale).

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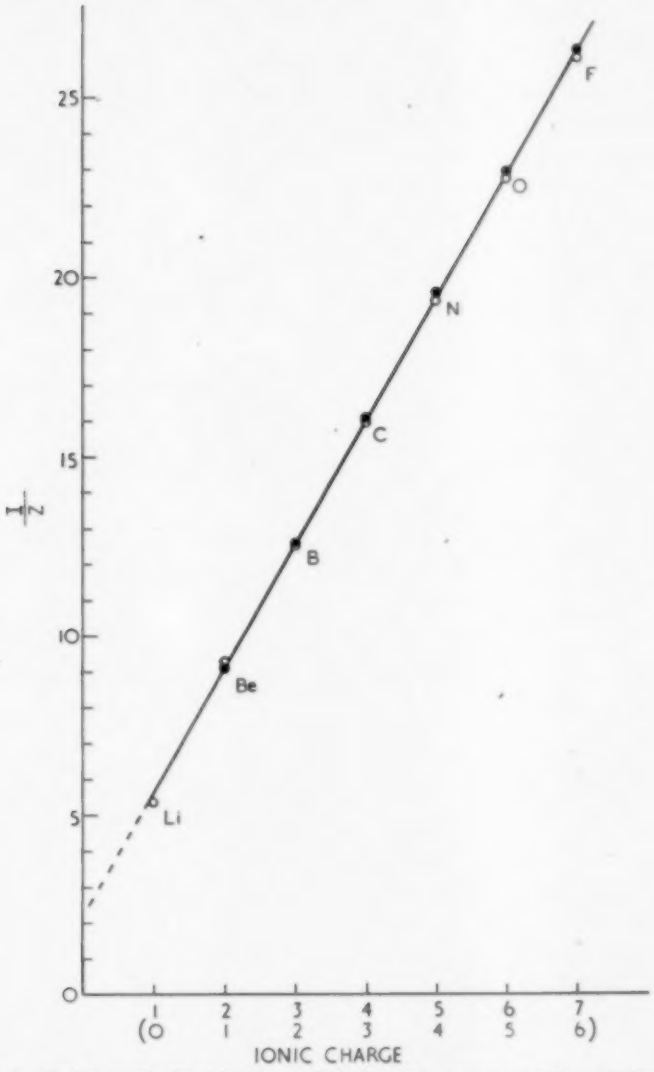

FIG. 8.—Variation of I_n/Z with Z in the $2s$ isoelectronic sequences, $Li^+ \rightarrow F^{7+}$ (open circles) and $Be^+ \rightarrow F^{6+}$ (full circles). Note scale displacement as in Fig. 7.

of 2·2 V ($=R'/5$) from 2·2 to 6·6 V ($=3R'/5$) where it appears to remain uniform for the 4*s* and 5*s* sequences.

For the 2*p* sequences, *a* remains uniform at ~3·5, but constant *b* increases first in two steps of 2·2–2·4 V and from N to O by only 0·6 V (note cross-over in Fig. 10), and finally in two steps of about 3 volts. Greater irregularities have been found in sequences involving 3*p* and 4*p* electrons, but as some of the ionization potentials are uncertain, these sequences will not be examined.

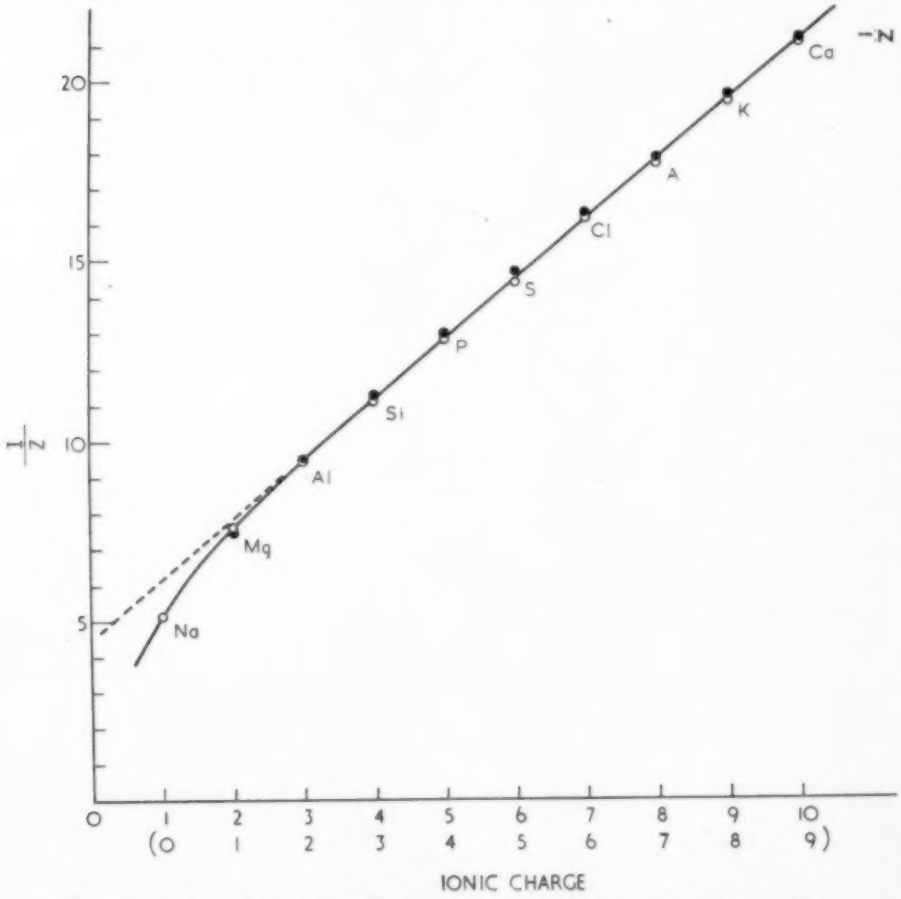

FIG. 9.—Variation of I_n/Z with Z in the 3*s* isoelectronics equences $Na^+ \rightarrow Ca^{19+}$ (open circles) and $Mg^+ \rightarrow Ca^{9+}$ (full circles). Note scale displacement as in Figs. 8 and 9.

Entry of d *electrons*

The first inner 3*d* electron enters at Sc and the 10 3*d* group is complete at Ni. During this development, 4*s* electrons remain on the outside of the atom, but after Ga (entry of first 4*p* electron) the 4*s* electron pair is pushed progressively deeper into the atom; Fig. 11 shows some ionization potential variations during these developments.

We will consider first the variation of $I_2/2$. From Ca to Ni (Ga), $I_2/2$ increases regularly with increase in N (number of electrons in N shell: for K, Ca, Sc; $N = 1$,

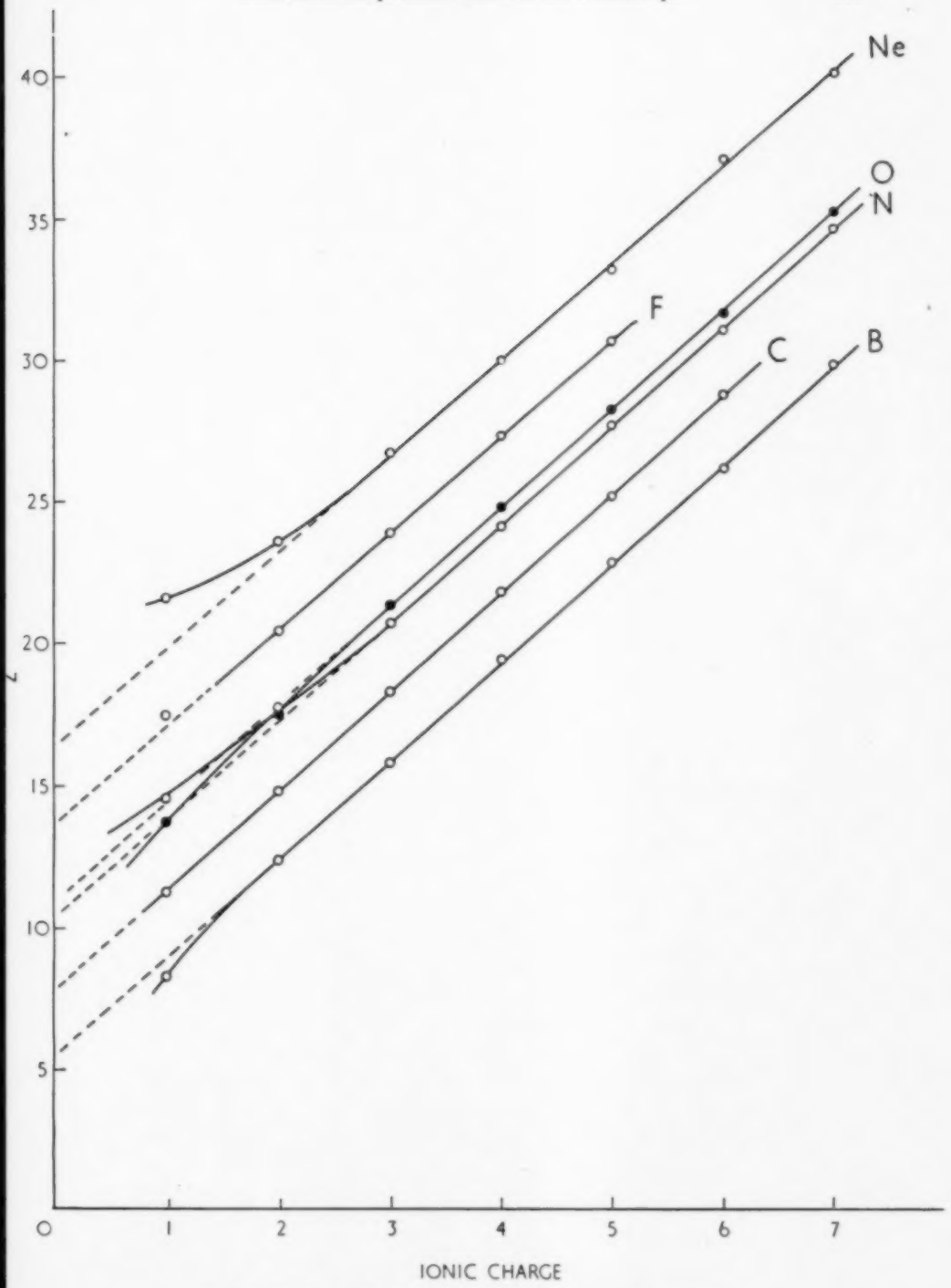

FIG. 10.—Variation of I_n/Z with Z in the $2p$ isoelectronic sequences;

$B^+ \rightarrow Na^{7+}$	(B)	$O^+ \rightarrow Si^{7+}$	(O–full circles)
$C^+ \rightarrow Na^{6+}$	(C)	$F^+ \rightarrow Al^{5+}$	(F)
$N^+ \rightarrow Al^{7+}$	(N)	$Ne^+ \rightarrow S^{7+}$	(Ne)

Note parallelism and N–O cross-over.

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2, 3, etc.). The relationship is almost linear, and the expression for the line as drawn is,

$$\frac{I_2}{2} = 0{\cdot}38N + 5{\cdot}2 \tag{3}$$

hence,

$$I_2 = 0{\cdot}76N + 10{\cdot}4. \tag{4}$$

Variation of I_1 is quite unlike that of $I_2/2$. It is fairly regular, but passes through a maximum and a minimum. Where the difference between I_1 and $I_2/2$ approaches a

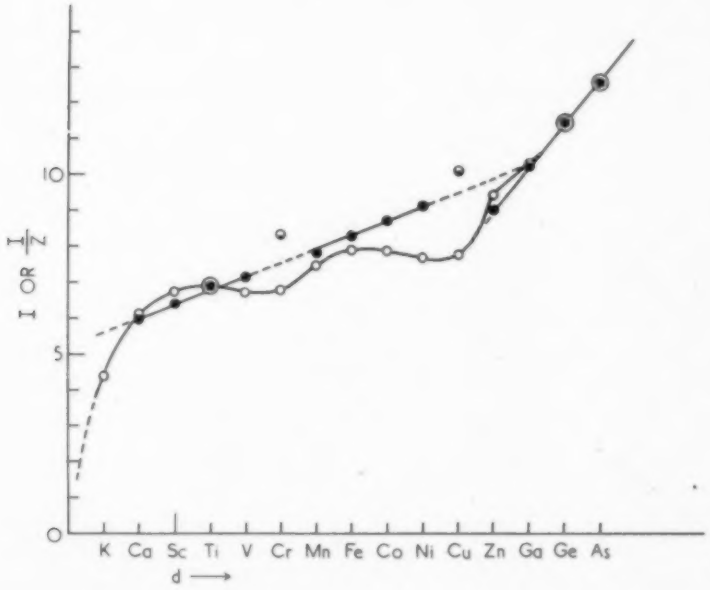

FIG. 11.—Effect of entry of 3*d* electrons on ionization potentials of 4*s* electrons.
(i) Variation of I_1 (K → Cu—open circles);
(ii) $I_2/2$ (Ca → Cu— full circles) and,
(iii) I_n/Z (Cu → As). In the third relationship n and $Z = 1, 2, 3, 4$, and 5 respectively for Cu, Zn, Ga, Ge, and As. In Cr and Cu, the second electron is a *d* electron and is indicated by a half-filled circle.

maximum, *d* electrons appear (Cr and Cu). A line joining these two points is of about the same slope as that of the principal regularity for $I_2/2$ vs. Z.

Constants a and b for the isoelectronic sequences $Cu^{+} \rightarrow Kr^{8+}$, $Zn^{1+} \rightarrow As^{4+}$, and $Sc^{3+} \rightarrow Fe^{8+}$ (*d* electrons) are given in Table 10.

Ionization potential variations over the range Rb → Te (Fig. 12) appear to be fairly irregular, although some of the developments do resemble K → As variations. Many of the data are, unfortunately, approximate. $I_2/2$ appears to vary linearly with N from Ru to Ag, perhaps also from Sr to Zr, and finally, apparent linear variation of I_n/Z along the isoelectronic sequences ($Ag^{+} \rightarrow I^{7+}$; $Cd^{+} \rightarrow I^{6+}$), as anticipated.

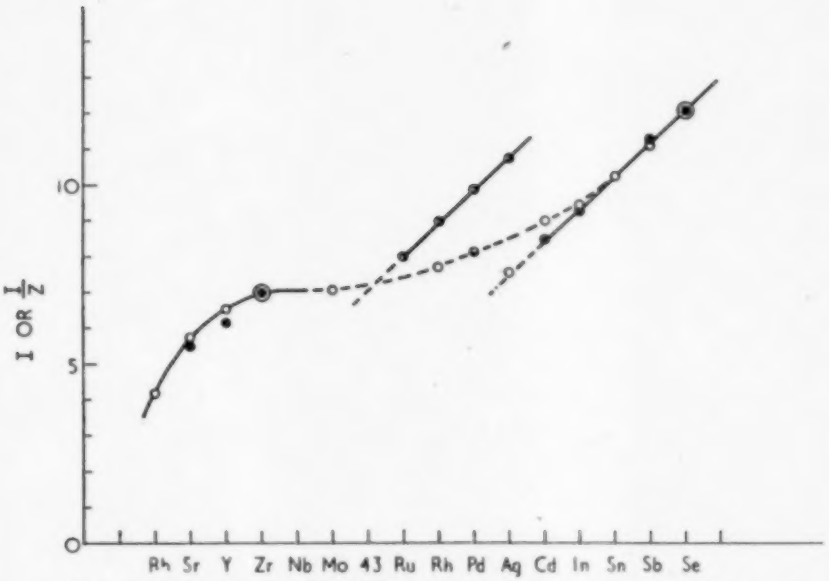

FIG. 12.—Ionization potential variations over the range Rb → Te (5*s* and 4*d* electrons).
open circle—I_1 (*s* electron)
half-filled circle (horizontal)—I_1 (*d* electron)
full circle—$I_2/2$ (*s* electron)
half-filled circle (vertical)—$I_2/2$ (*d* electron).

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PART III

SOME RELATIONSHIPS BETWEEN IONIC RADIUS, IONIZATION POTENTIAL, AND IONIC CHARGE

Variation of I_n with r (8-electron cations only) in the Periodic Table is shown in Fig. 13. Regularities are well developed and smooth along isoelectronic sequences, and also in the vertical groups Na^+—K^+—Rb^+—Cs^+ and Mg^{2+}—Ca^{2+}—Sr^{2+}—Ba^{2+}, where the relationship

$$I_n \propto \frac{1}{\sqrt{r}} \qquad (Z \text{ constant})$$

is closely approximated.[2] Entry of 3*d* electrons (Sc) disturbs this relationship; deviation increases progressively along the sequence, $Sc^{3+} \rightarrow Mn^{7+}$ and the *n*th ionization potentials of V, Cr, and Mn are actually greater than the equivalent ionization potentials (5th, 6th, and 7th, respectively) of P, S, and Cl, despite the fact that the radii of P^{5+}, S^{6+}, and Cl^{7+} are considerably smaller than the radii of the corresponding cations, V^{5+}, Cr^{6+}, and Mn^{7+}. These developments are shown more clearly in Fig. 14, which has been traced from Fig. 13. Entry of 4*f* electrons causes the well-known lanthanide contraction (Fig. 14), illustrated also in Fig. 15, a plot of r vs. ionic charge. Despite considerable contraction from La^{3+} (1·15 A) to Lu^{3+} (0·85 A), the third ionization potential of Lu (~19 V) is apparently about the same as the third ionization potential of La. (The third ionization potential of Sc ($r = 0{\cdot}81$ A) is

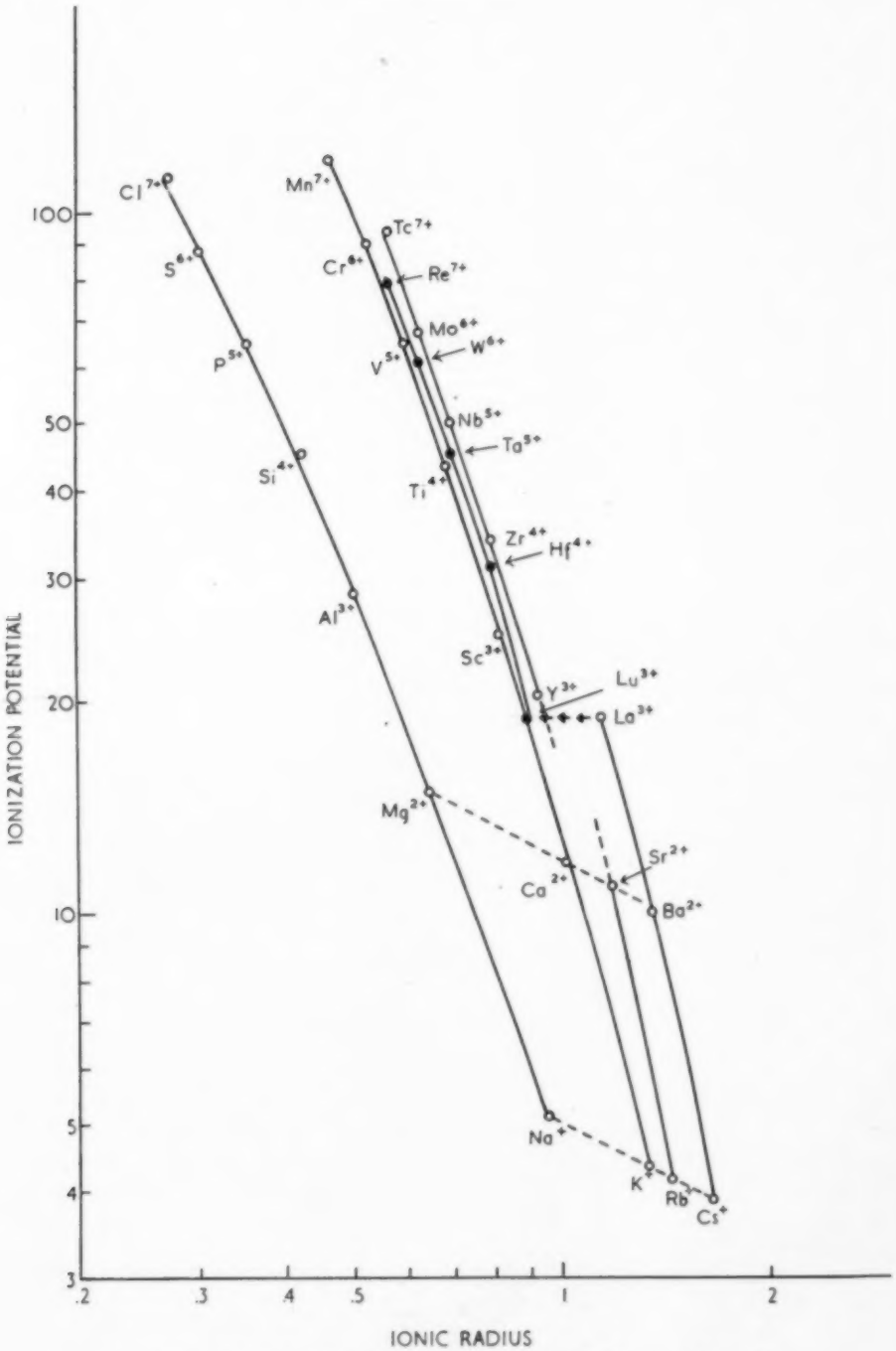

FIG. 13.—Variation of r and I_n in isoelectronic sequences (8-electron cation only).

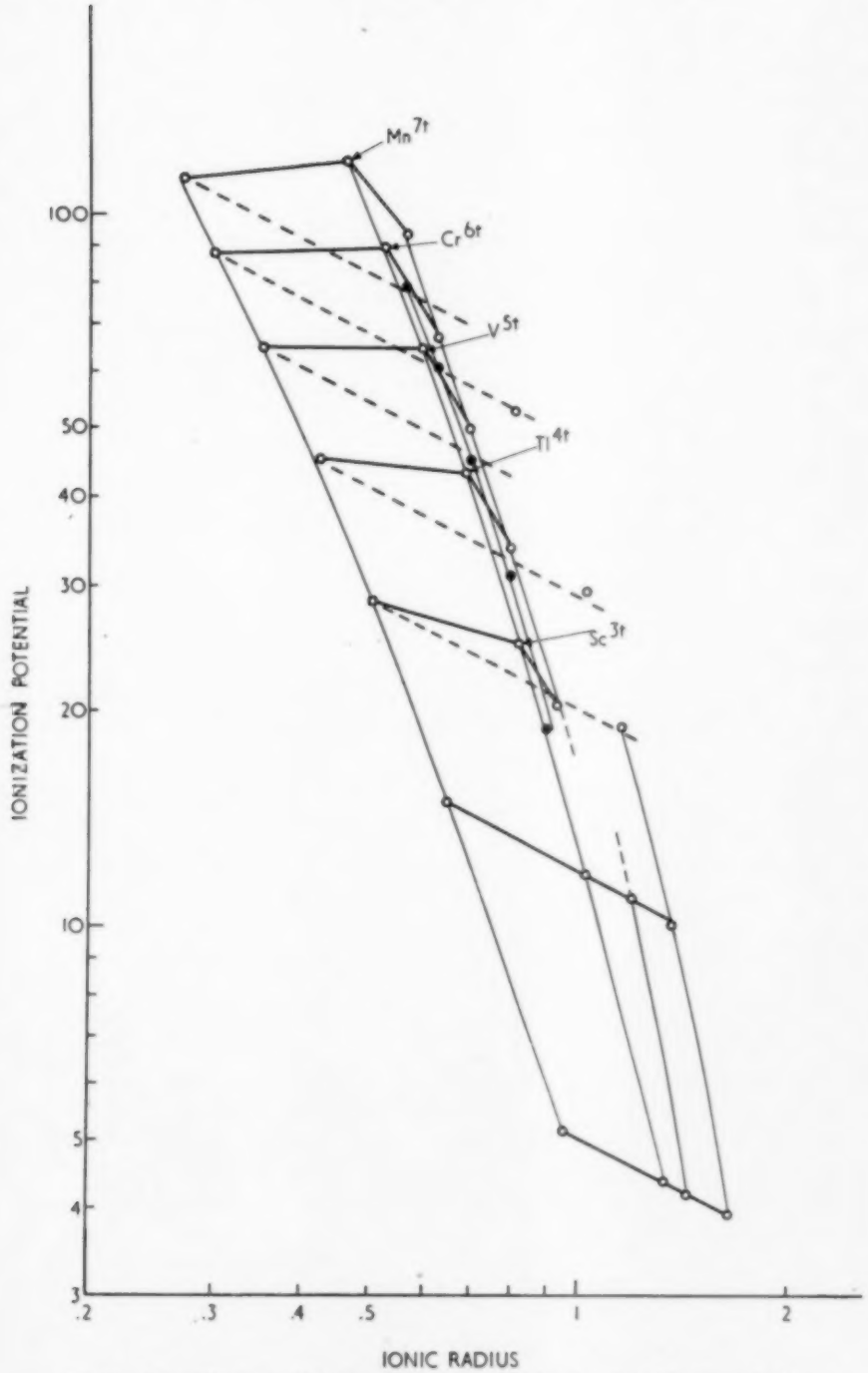

FIG. 14.—Traced from Fig. 13 for the purpose of emphasizing elevation of I_n as a result of entry of 3*d* electrons. Lines through members of $Na^+ \rightarrow Cl^{7+}$ sequence are parallel, with slope of 26·5°, the tan of which is ½. Note fit in vertical groups Na^+, K^+, Rb^+, and Cs^+; Mg^{2+}, Ca^{2+}, Sr^{2+}, and Ba^{2+}.

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much higher, namely, 24·8 V; see Fig. 13). The sequence Hf^{4+}—Ta^{5+}—W^{6+} follows entry of 4*f* electrons, and the radii of these cations are virtually identical with the corresponding cations Zr^{4+}—Nb^{5+}—Mo^{6+}; however, the *n*th ionization potentials of the heavier cations are distinctly lower than those of the corresponding lighter cations (Fig. 13).

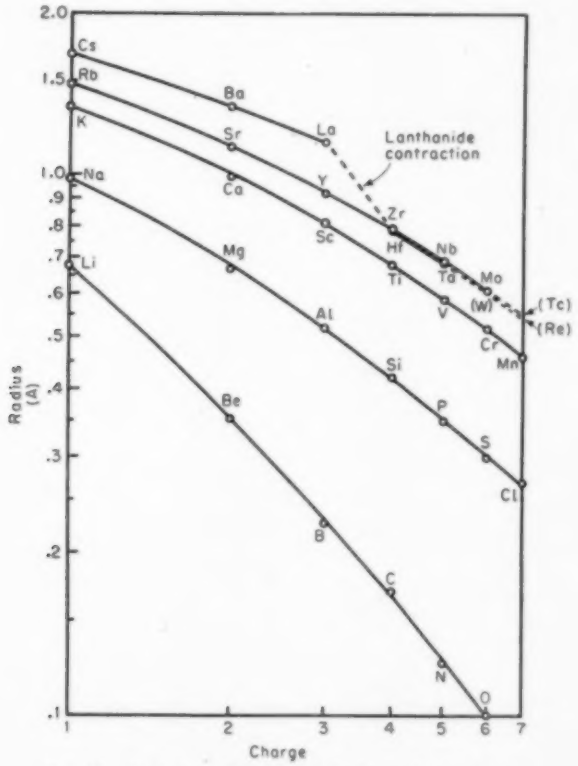

FIG. 15.—Variation of *r* with *Z* in isolectronic sequences.

I_n vs. *r* relationships in the 18-electron cations of isoelectronic sequences are shown in Fig. 16. Regularities are again smooth, and, in general, ionization potentials are elevated when compared with 8-electron (non-transitional) cations, of equivalent size and charge. Greatest elevation of ionization potential follows the entry of 4*f* electrons, and instead of a regular decrease of ionization potential with increase in size, in the groups Cu^+ (0·91 A)—Ag^+ (1·26 A)7 A)—Au^+ (1·3 and Zn^{2+} (0·69 A)—Cd^{2+} (0·97 A)—Hg^{2+} (1·10 A), the *n*th ionization potentials, of Au and Hg are actually greater than those of Cu and Zn respectively. Ionization potential elevation progressively decreases, however, along isoelectronic sequences. These developments may be examined more closely in Fig. 17, after AHRENS,[2] which includes nearly all elements. (Some of the plotted points in Fig. 17 differ slightly from those in Fig. 13, as they were based on older data; the main features are the same.)

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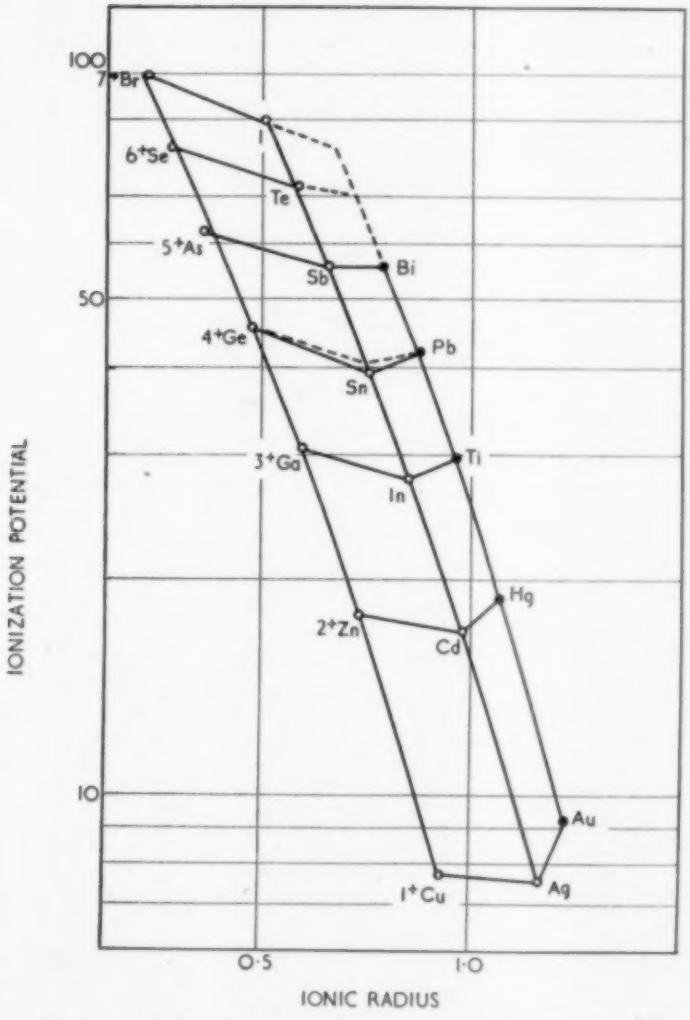

FIG. 16.—Variation of r with I_n in isoelectronic sequences involving 18—electron cations. Note location of members of the $Au^{+} \rightarrow Bi^{3+}$ sequence.

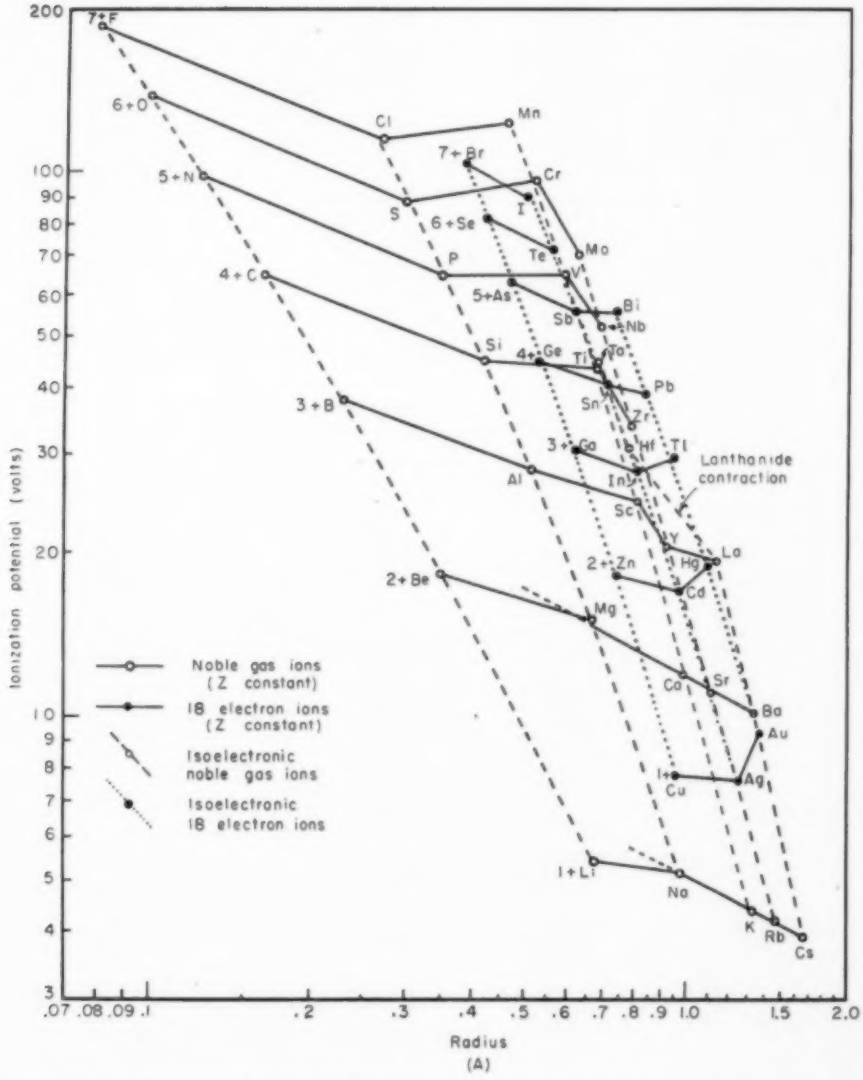

FIG. 17.—A comparison of variation of r with I_n for 2-, 8-, and 18-electron sequences.

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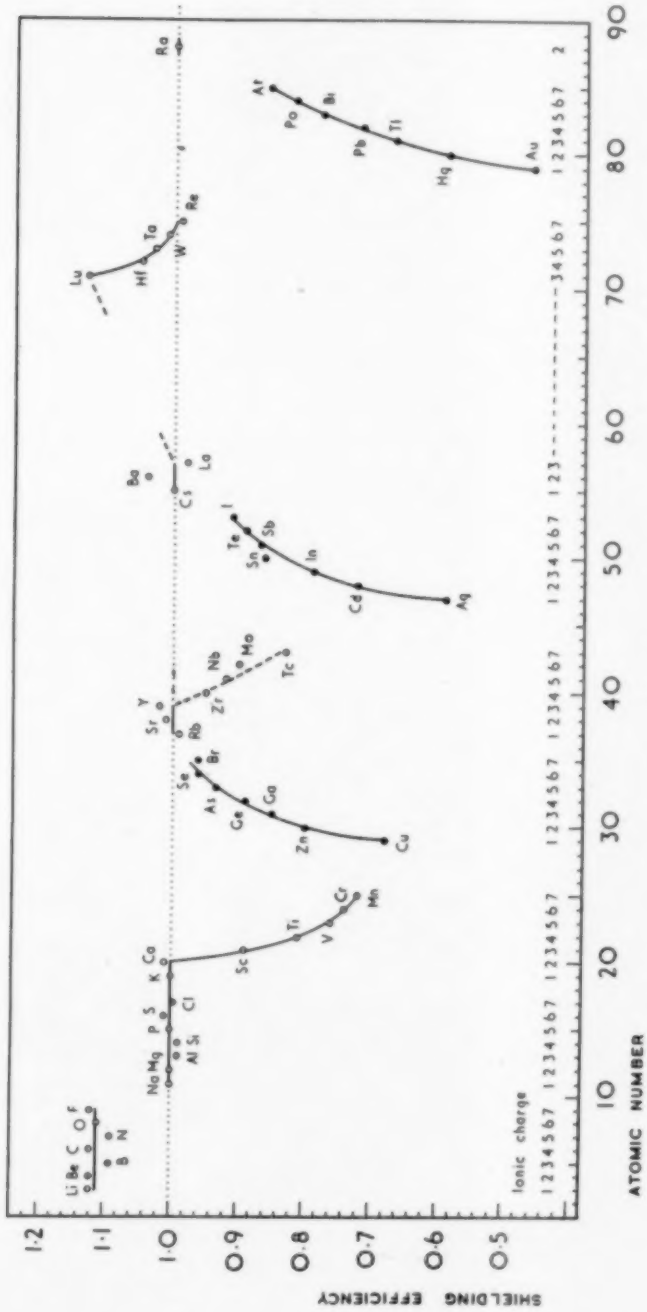

FIG. 18.—Variation of the quantity $SZ^{1\cdot47}/I_n\sqrt{r}$, a suggested measure for comparing shielding efficiency in successive isoelectronic sequences.

It has been found[4] that the relationship

$$5Z^{1\cdot27} = I_n\sqrt{r}$$

is quite closely approximated by nontransitional 8-electron cations (alkali metal cations; alkaline earth cations and members of the sequence $Na^+ \rightarrow Cl^{7+}$). For these cations the ratio,

$$\frac{5Z^{1\cdot27}}{I_n\sqrt{r}}$$

should be unity ($\pm$ a small tolerance), but, for other cations values ranging from 1·15 to 0·45 are found. Fig. 18 relates this ratio to atomic number; the value of the ratio either remains uniform ($Li^+ \rightarrow F^{7+}$; $Na^+ \rightarrow Cl^{7+}$), or swings smoothly away from ($Sc^{3+} \rightarrow Mn^{7+}$, for example, the entry of 3*d* electrons), or towards ($Cu^+ \rightarrow Br^{7+}$, for example) a value of unity. AHRENS[4] has suggested that the above ratio may be used as a measure for comparing the shielding (screening) efficiency of cations, and has referred to the usefulness of this concept and ionization potentials in general, for understanding more closely a variety of properties of elements and their compounds. A few have been discussed in some detail,[3] and discussions of others are in preparation.

Acknowledgement—The writer has benefited much from discussions with Professors C. A. COULSON and M. H. L. PRYCE.

J. Inorg. Nucl. Chem., 1956, Vol. 2, pp 315 to 322. Pergamon Press Ltd., London

THE ELECTRONIC STRUCTURES OF SOME MIXED COMPOUNDS OF CYCLOPENTADIENYL AND CARBON MONOXIDE OR NITRIC OXIDE WITH THE TRANSITION METALS

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(*Received* 17 *January* 1956)

Abstract—The electronic structures of some mixed compounds of cyclopentadienyl and carbon monoxide or nitric oxide with the transition metals are described in terms of molecular-orbital theory. It is shown that the most stable compounds possess eighteen valence electrons.

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RECENTLY the preparation of a number of mixed cyclopentadienyl carbonyl compounds of the transition metals and of some closely related nitrosyls has been reported.[1, 2] The simplest of these compounds, $(C_5H_5)V(CO)_4$, $(C_5H_5)Mn(CO)_3$, $(C_5H_5)Co(CO)_2$, and $(C_5H_5)Ni(NO)$, will be discussed in this paper. FISCHER has noted that all of these compounds are diamagnetic, and has pointed out that this can be explained if we suppose that the cyclopentadienyl radical contributes five electrons to the metal, which thereby attains the rare-gas configuration with eighteen electrons. PIPER *et al.*, on the other hand, have suggested that each cyclopentadienyl radical contributes only one electron to the metal atom, which then has a share in fourteen electrons. We have examined this problem by the molecular-orbital method developed in previous papers,[3, 4, 5, 6] and have concluded that, in that theory, only the former point of view is tenable.

We consider first the simplest of these compounds $(C_5H_5)_5Ni(NO)$, which we presume to have C_{5V} symmetry. If the Ni, N, and O atoms are not collinear, our treatment requires some modification, but the conclusions remain substantially unchanged. The classification of orbitals according to symmetry types is given in Table 1. The only feature of this table which has not been discussed previously is the inclusion of the nitric oxide orbitals. We have considered only two of these, namely the unshared σ orbital on the nitrogen atom which transforms as a_1, and the antibonding π orbital which transforms as e_1. We have neglected the bonding e_1 orbital on the nitric oxide, since its inclusion would make no difference to the subsequent analysis. In all we have to dispose of eighteen electrons, five from the cyclopentadienyl radical, ten from the iron atom, and three from the nitric oxide molecule. We shall show that the correct electronic configuration is almost certainly

$$(a_1')^2\,(a_1'')^2\,(a_1''')^2\,(e_1')^4\,(e_1'')^4\,(e_2')^4. \qquad (1)$$

[1] T. S. PIPER, F. A. COTTON, and G. WILKINSON, *J. Inorg. Nucl. Chem.* **1**, 165 (1955).
[2] E. O FISCHER and H. LEIPFINGER, *Z. f. Naturforsch.* **106**, 353 (1955).
[3] J. D. DUNITZ and L. E. ORGEL, *Nature* **171**, 121 (1953).
[4] IDEM, *J. Chem. Phys.* **23**, 954 (1955)
[5] W. MOFFITT, *J. Amer. Chem. Soc.* **76**, 3386 (1954).
[6] H. H. JAFFE, *J. Chem. Phys.* **21**, 156 (1953).

We denote orbitals of the complete molecule by symbols such as a_1' or e_1'', where the number of primes indicates the sequence of energies.

The distribution of electrons in the two e_2 orbitals presents no difficulty. One

TABLE 1.—SYMMETRY CLASSIFICATION FOR $(C_5H_5)Ni(NO)$

		Metal	Cyclopentadienyl	Nitric oxide
a_1	stable	s, d_{z^2}	a_1	σ
	unstable	p_z	—	—
e_1	stable	d_{xz}, d_{yz}	e_1	—
	unstable	p_x, p_y	—	π
e_2	stable	d_{xy}, $d_{x^2-y^2}$	—	—
	unstable	—	e_2	—

degenerate molecular orbital, made up mainly from metal d_{xy} and $d_{x^2-y^2}$ orbitals mixed perhaps with a little of the cyclopentadienyl e_2 orbital, is a stable bonding orbital and contains four electrons. The other is required by orthogonality to consist

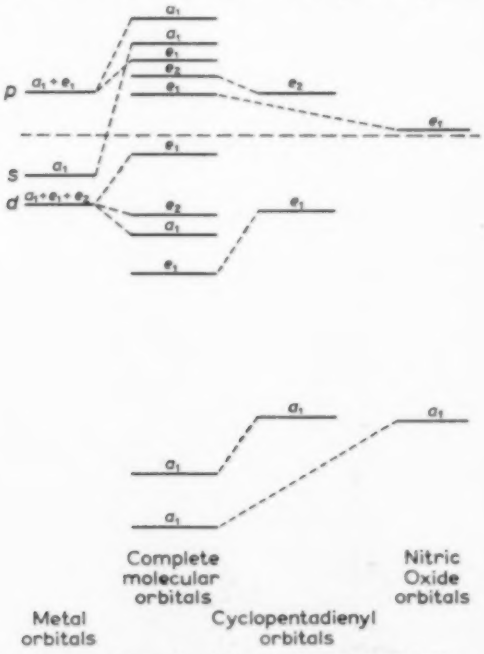

FIG. 1.—Energy-level diagram for $(C_5H_5)Ni(NO)$.

mainly of the unstable cyclopentadienyl e_2 orbital mixed with a little of the metal orbitals. It is antibonding and unstable, and is empty in the ground state of the molecule. A diagrammatic energy-level scheme for these and for the other molecular orbitals is shown in Fig. 1.

The forms and stabilities of the a_1 orbitals are not dealt with so easily. It is quite clear that two of these, made up mainly from the a_1 orbital of the cyclopentadienyl ring and the unshared pair orbital on the nitrogen atom, are very stable and certainly filled. They are both bonding orbitals and correspond to the lowest, very stable a_{1g} and a_{1u} orbitals of the bis-cyclopentadienyls. There are two arguments, one theoretical and one empirical, which show that a third a_1 orbital is occupied.

In addition to the stable a_1 orbitals of the cyclopentadienyl radical and the nitric oxide molecule, there are two stable orbitals on the metal atom, the $3d_{z^2}$ and the $4s$, which are occupied in the free atom. MOFFITT[5] has suggested that these orbitals are mixed together in the field of a pair of cyclopentadienyl radicals in such a way as to give one very stable orbital and one unstable orbital. It has also been shown that simple molecular-orbital theory leads one to expect a fairly stable orbital of this kind.[4] In the nitric oxide compound a similar mixing between $3d_{z^2}$ and $4s$ orbitals is to be expected, and in addition the lower of the resulting orbitals may be further stabilized by mixing with the $4p_z$ orbital. Thus the arguments for the existence of a third occupied a_1 orbital are at least as strong in this case as they are for, say, ferrocene.

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The second argument is more nearly conclusive. The diamagnetism of the molecule indicates that there are no partially filled orbitals. Since eighteen electrons are present in all, and since all orbitals are nondegenerate (a_1) or doubly degenerate (e_1, e_2), there must be an odd number of occupied a_1 orbitals. We have shown that this must be greater than two, and since there are certainly not as many as five stable a_1 orbitals, we are forced to conclude that three a_1 orbitals are occupied.

In this compound, as in the bis-cyclopentadienyls, the nature of the e_1 orbitals is critical to an understanding of the chemical properties, and so it must be discussed in detail. The e_1 orbitals are now very different from those present in the bis-cyclopentadienyls, on account of the low electron affinity of the nitric oxide π-orbital. This is indicated in Fig. 1. The experimental evidence for the electron affinity of the e_1 orbital of nitric oxide being lower than that for cyclopentadienyl is quite unambiguous. While cyclopentadiene readily forms an anion containing four e_1 electrons, nitric oxide tends to lose its single π electron and only acquires a second one under exceptional conditions.

We thus have available for the formation of e_1 molecular orbitals a stable e_1 orbital on the cyclopentadienyl, a stable e_1 orbital on the metal atom, an unstable e_1 ($4p_x$, $4p_y$) orbital on the metal atom, and an unstable π orbital on the nitric oxide. Clearly the most stable e_1 molecular orbital will be made up of a bonding combination of the metal and cyclopentadienyl orbitals, but the important question of the nature of the metal orbital remains. This should be mainly $3d$ in character, but owing to the possibility of $3d_\pi$-$4p_\pi$ hybridization[7,8] we expect a good deal of the $4p$ orbital to be mixed in. This orbital is shown diagrammatically in Fig. 2(a). d_π-p_π hybridization should be quite important in stabilizing the metal-cyclopentadienyl bond, and has some further important consequences.

The second stable e_1 orbital must consist mainly of metal $3d$ and $4p$ orbitals, and partly of the nitric oxide orbital. The requirement of orthogonality automatically forces it away from the cyclopentadiene ring and towards the nitric oxide molecule, thus facilitating the formation of a fairly strong double bond (see Fig. 2b). The

[7] D. P. CRAIG, A. MACCOLL, R. NYHOLM, L. E. ORGEL, and L. E. SUTTON, *J. Chem. Soc.*, 332 (1954).
[8] J. CHATT, *Symposium on Co-ordination Chemistry*, Copenhagen 1953.

remaining e_1 orbitals are expected to be unstable, and since there are not enough electrons available to fill either of them, we need not consider them further.

We have shown that the stability of $(C_5H_5)Ni(NO)$ can be understood on molecular orbital theory, if it is assumed that in all eighteen electrons are involved in the bonding

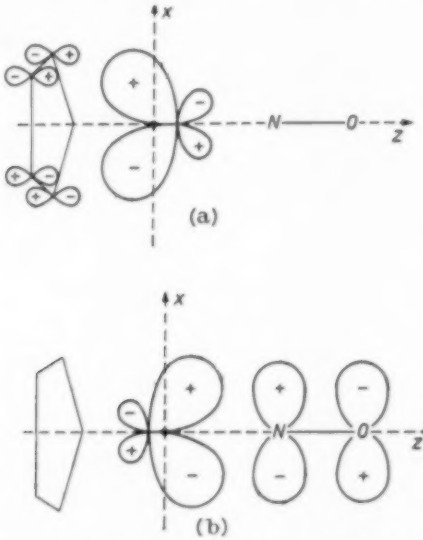

FIG. 2.—The x components of the two bonding e_1 orbitals in $(C_5H_5)Ni(NO)$.

system. We must next ask whether it is possible to understand the structure on the basis of only fourteen electrons being available to the metal. We think not, for the only reasonable assignment consistent with the diamagnetism of the system would be

$$(a_1')^2\,(a_1'')^2\,(a_1''')^2\,(e_1')\,(e_2')^4. \tag{2}$$

This is easily seen to be true, since the assignment $(a_1')^2\,(a_1'')^2\,(a_1''')^2\,(e_1')^4\,(e_1')^4$ implies the presence of four vacancies in the $3d$ shell, namely in the $3d_{xy}$ and $3d_{x^2-y^2}$, and this is quite implausible. Similarly, the configuration $(a_1')^2\,(e_1')^4\,(e_1'')^4\,(e_2')^4$ can be ruled out. If we accept assignment (2), we must identify e_1' with metal orbitals, and discount the other four e_1 electrons. This, however, is equivalent to denying the existence of a sandwich bond, which goes against the available experimental evidence.

There is a further objection to the suggestion that the cyclopentadienyl group supplies only one electron, namely the failure to prepare stable compounds such as $(C_5H_5)Ni(NO)(CO)_2$. It is one of the most remarkable features of the chemistry of the transition-metal carbonyls etc. that all of the available $3d$, $4s$, and $4p$ orbitals are employed, e.g. in $Co(NO)(CO)_3$. If the cyclopentadienyl radical contributed only one electron to the bonding system, the nonexistence, e.g., of $(C_5H_5)Co(CO)_4$ would be a mystery. Our molecular-orbital treatment provides a simple and natural explanation of the empirical formulae of this and, as we shall see, all the other mononuclear compounds. In the particular case of $(C_5H_5)Ni(NO)$, the $4p_x$ and $4p_y$ orbitals are already partially occupied, and a high concentration of electron density has been built up in just those regions of space where the unshared pairs of carbon monoxide

molecules would have to go if they were to add on to the metal. Under these circumstances further addition of carbon monoxide is unlikely to lead to stable complexes.

PIPER *et al.*[1] are not necessarily incorrect in describing these systems in terms of a valence shell of fourteen electrons, for the definition of the valence shell is to some extent arbitrary. However, within the framework of the *molecular-orbital* method, there is no natural description of the compounds in which only one of the three e_1 electrons of the cyclopentadienyl is included in the valence shell.

In our treatments of the compounds containing more than one carbon monoxide molecule we shall usually neglect metal-carbon double bonding, not because it is unimportant, but because of the complication which it would introduce. Its function is to remove the excess negative charge which would otherwise accumulate on the metal ion as the number of carbon monoxide molecules in the complex increased. The extension of the theory which is required to take it into account is quite straightforward in principle, but in practice the number of orbitals which have to be considered soon becomes very large. The spectroscopic evidence suggests that the extent of double bonding is comparable to that in the simple metal carbonyls. We shall accept the structures proposed by PIPER *et al.* for the various carbon monoxide compounds.

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The total symmetry of $(C_5H_5)Mn(CO)_3$ is very low. In fact, there is no symmetry unless the three carbon monoxide molecules are exactly in the staggered or eclipsed configurations relative to the cyclopentadienyl ring. However, an approximate classification of orbitals is still possible. In the group C_{3V} of the $Mn(CO)_3$ fragment of the molecule, the three orbitals on the carbonyl carbon atoms transform as a and e. These orbitals have just the correct forms to combine with the a_1 and e_1 orbitals of the cyclopentadienyl, and with the metal orbitals classified as a_1 and e_1 in Table 1. This is an accident depending on the shapes of the various orbitals. It is *not* a group theoretical necessity. Furthermore, there is reason to expect that the other d orbitals, d_{xy} and $d_{x^2-y^2}$, also transforming as e in the C_{3V} group, will not mix seriously with the others. Under these circumstances the approximate orbital classification in

TABLE 2.—APPROXIMATE SYMMETRY CLASSIFICATION FOR $(C_5H_5)Mn(CO)_3$

		Metal	Cyclopentadienyl	Carbon monoxide
a_1	stable	s, d_{z^2}	a_1	a_1
	unstable	p_z	—	—
e_1	stable	d_{xz}, d_{yz}	e_1	e_1
	unstable	p_x, p_y	—	—
e_2	stable	d_{xy}, $d_{x^2-y^2}$	—	—
	unstable	—	e_2	—

Table 2 is possible. It will be seen that the only serious difference from Table 1 occurs in the e_1 orbitals. The unstable, normally empty orbital of nitric oxide has been replaced by a stable, normally filled orbital on the three carbon monoxide groups.

In this and the subsequent discussion we have not used the strict group-theoretical notation for the molecular orbitals, since it is only by preserving the same labels for

corresponding orbitals of all the compounds, independent of their total symmetry, that we can emphasize the features of the electronic structure which are common to the whole set.

In Fig. 3 we show diagrammatically the energy-level scheme for the e_1 orbitals. As before, we have two stable and two unstable e_1 orbitals, but now one of the stable orbitals is concentrated largely on the carbon monoxide groups. This situation is

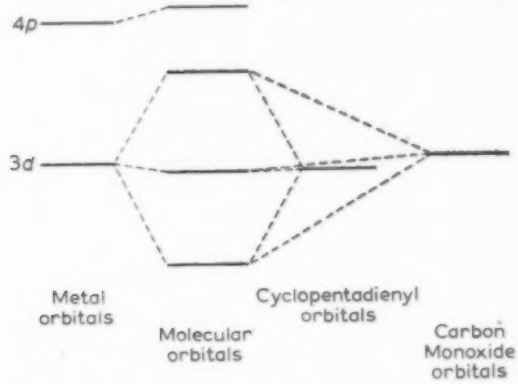

FIG. 3.—Energy-level diagram for the e_1 orbitals of $(C_5H_5)Mn(CO)_3$.

almost identical with that previously discussed for the bis-cyclopentadienyls, the a_1 and e orbitals of the carbon monoxide molecules corresponding in form to the a_1 and e_1 orbitals of cyclopentadienyl. The only difference in our treatment is the explicit inclusion of the $4p$ orbitals necessitated by the asymmetry of the field acting on the

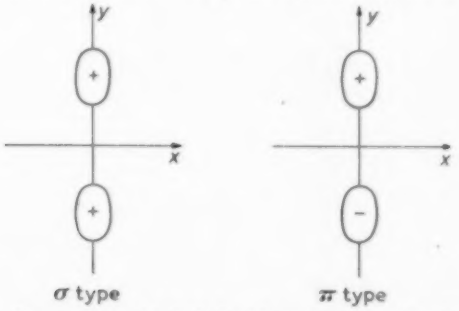

FIG. 4.—The σ and π orbitals derived from the two unshared pairs of the carbon monoxide molecules in $(C_5H_5)Co(CO)_2$.

metal atom. (The energy-level diagram indicates clearly why compounds such as $(C_5H_5)Ni(NO)(CO)_2$ would be less stable.) The final approximate configuration, just as for $(C_5H_5)Ni(NO)$, is

$$(a_1')^2\,(a_1'')^2\,(a_1''')^2\,(e_1')^4\,(e_1'')^4\,(e_2')^4$$

In $(C_5H_5)Co(CO)_2$ the degeneracy of certain of the orbitals which would be classified as e_1 or e_2 in more symmetrical molecules is completely removed. We suppose that the two carbon monoxide molecules lie in the yz plane. Their unshared σ orbitals combine to form a σ and a π_y type molecular orbital (Fig. 4), each of which is very stable. The corresponding π_x orbital is very unstable, since it is made up from

the normally empty π orbitals of the carbon monoxide molecules. Once again the orbitals which differ most from those of the more symmetrical molecules are those corresponding to the e_1 orbitals. The π_x orbitals behave like the e_1'' orbitals of $(C_5H_5)Ni(NO)$ and the π_y orbitals like the e_1'' orbitals of $(C_5H_5)Mn(Co)_3$. This follows since all the arguments given for the e_1'' orbital of $(C_5H_5)Ni(NO)$ transfer directly to the π_x orbitals, and those given for the e_1 orbital of $(C_5H_5)Mn(CO)_3$ to the π_y orbital. The orbital assignment may be written

$$(a_1')^2\,(a_1'')^2\,(a_1''')^2\,(e_{1x}')^2\,(e_{1y}')^2\,(e_{1x}'')^2\,(e_{1y}'')^2\,(e_2')^4$$

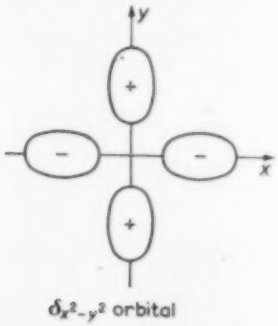

FIG. 5.—The $d_{x^2-y^2}$ orbital of the four unshared pairs of the carbon monoxide molecules in $(C_5H_5)V(CO)_4$.

In this assignment we write (e_{1x}') for the x component of the orbital corresponding to the e_1 orbital of the more symmetrical molecules.

In our treatment of $(C_5H_5)Co(CO)_2$ we neglected the effect of the two carbon monoxide groups on the degeneracy of the e_2 orbitals because it is not of particular importance. In our final and most difficult example $(C_5H_5)V(CO)_4$ this is no longer justifiable.

Let us suppose that the four carbon monoxide molecules lie in the xz and yz planes. Their unshared pairs combine to give one σ-type orbital, and a pair of equivalent π-type orbitals and an orbital whose shape corresponds to that of a $d_{x^2-y^2}$ orbital (Fig. 5). The discussion of the σ and π-type orbitals follows exactly that given for the a_1 and e_1 orbitals of $(C_5H_5)Mn(CO)_3$. The presence of the orbital which can combine with the $d_{x^2-y^2}$ orbital on the metal now completely removes the degeneracy of the d_{xy} and $d_{x^2-y^2}$ metal orbitals. The former orbital is occupied just as before, but the latter is destabilized by interaction with the corresponding carbon monoxide orbital, and so is empty. The electron configuration is exactly the same as for $(C_5H_5)Mn(CO)_3$, except that the e_2 orbital containing four electrons is split into two nonequivalent occupied orbitals

$$(e_2)^4 \rightarrow (e_{x^2-y^2})^2\,(e_{xy})^2.$$

We have considered the various compounds in order of increasing complexity of their molecular-orbital formulation. If we now take them in the more natural sequence, $(C_5H_5)Ni(NO)$, $(C_5H_5)Co(CO)_2$, $(C_5H_5)Mn(CO)_3$, $(C_5H_5)V(CO)_4$, suggested by their composition, we can discern more readily the general features which govern their electronic structure. All of the electron assignments are based on the fundamental assignment,

$$(a_1')^2\,(a_1'')^2\,(a_1''')^2\,(e_1')^4\,(e_1'')^4\,(e_2')^4$$

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for compounds with C_5 symmetry. The nature of the a_1 orbitals differs only slightly from compound to compound and requires no further discussion. The e_1'' orbital is predominantly a metal orbital in $(C_5H_5)Ni(NO)$ (and would be even more so in the hypothetical $(C_5H_5)CuCO$ molecule). As the atomic number of the metal decreases, and the number of carbon monoxide molecules increases, it changes to a predominantly ligand orbital in two stages. In $(C_5H_5)Co(CO)_2$ only one component is still mainly a metal orbital, and by $(C_5H_5)Mn(CO)_3$ both components are very largely derived from the ligands. In $(C_5H_5)V(CO)_4$ the same type of charge begins to affect the e_2' orbital, one component of which ceases to be an almost entirely nonbonding metal $d_{x^2-y^2}$ orbital and is replaced by a bonding orbital, largely on the carbon monoxide molecules. These features of the electronic structure are illustrated in Table 3. The stability of

TABLE 3.—VERY APPROXIMATE ELECTRON DISTRIBUTIONS IN MIXED CYCLOPENTADIENYLS

	$(C_5H_5)Ni(NO)$	$(C_5H_5)Co(CO)_2$	$(C_5H_5)Mn(CO)_3$	$(C_5H_5)V(CO)_4$
a_1'''	M^2	M^2	M^2	M^2
e_1'	$M(C_5H_5)^3$	$M(C_5H_5)^3$	$M(C_5H_5)^3$	$M(C_5H_5)^3$
e_1''	$M^3(NO)$	$M^2(CO)^2$	$(CO)^4$	$(CO)^4$
e_2'	M^4	M^4	M^4	$M^2(CO)^2$

The superscripts give the numbers of electrons provided by the different components (M = metal atom)

the inert-gas structure for these compounds is seen, in molecular-orbital theory, to depend on the constancy of the number of moderately stable orbitals of a given approximate symmetry class, even when the electronegative centre is shifted away from the metal to the ligands. We shall show in a later paper that this general feature of the electronic structure of transition-metal carbonyls, acetylene compounds, etc. has a considerable predictive value.

While the closed-shell structure with eighteen valence electrons is usual for the neutral compounds of this type, $[Fe(C_5H_5)(CO)_2]^{++}$ with only sixteen electrons has been prepared. This raises the general question of the stability of compounds with less than eighteen *d* electrons. We believe that the most stable ions of this type will be found to be derived from neutral compounds containing e_1 electrons which are essentially in atomic d_π–p_π hybrids, e.g. $M(C_5H_5)CO$, $M(C_5H_5)NO$, and $M(C_5H_5)(CO)_2$. Furthermore, in these cases, the stability of the systems with less than eighteen electrons will be favoured by a large 3*d*–4*p* energy separation, since the filling of the e_1'' orbital involves some 3*d*–4*p* promotion. This leads us to expect that, for example, the sixteen electron systems will be somewhat more stable relative to the eighteen electron systems if the metal ion carries a positive charge.

Acknowledgements—The author is indebted to Dr. J. D. DUNITZ for his most helpful comments on the manuscript, and to Professor H. C. LONGUET-HIGGINS for several discussions.

J. Inorg. Nucl Chem., 1956, Vol. 2, pp. 323 and 324. Pergamon Press Ltd., London

PARACHOR AND π-BONDING RELATIONSHIPS IN SILICON COMPOUNDS

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(*Received* 25 *January* 1956)

Abstract—It is proposed that the presence of π-bonding in silicon compounds may be inferred if "polar" Si-H bond parachors must be used to obtain agreement between calculated and experimental molecular parachors.

The surface tension of disilyl sulphide has been measured *in vacuo* and has been found to be 22·31 dynes/cm at 18°C. The experimental parachor has a value of 221·3 at this temperature and the Si-S bond parachor a value of 23·4.

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To obtain agreement between experimental and calculated values of the parachor for many silicon compounds, it has been necessary to introduce two sets of Si-H bond parachors. The "polar" Si-H bond parachor value must be employed in compounds where a fluorine, chlorine, or oxygen atom is attached to the silicon, while the "non-polar" Si-H bond parachor is used in other cases, e.g. when an iodine atom is attached to the silicon.[1] The necessity of having two sets of Si-H bond parachors cannot be due to purely inductive causes, since it is not necessary to have two values for the C-H bond parachor.[2]

It has been pointed out in recent papers[3, 4, 5] that Si-F, Si-Cl, Si-O, and Si-S linkages often have considerable double or π-bond character, e.g. $\equiv$Si$\leftarrow$F, whereas many other silicon bonds, e.g. $\equiv$Si—I have little or none. It is here proposed that the presence of π-bonding in a linkage is expressed by the Si-H bond parachor in the compound; viz., those compounds for which the polar Si-H bond parachor must be used have much π-bonding involved in their other linkages, and those for which the nonpolar Si-H bond parachor must be used have no, or very little π-bonding character. If this postulate is valid, then the parachor of a silicon compound could be used as an empirical physical method for determining the presence of π-bonds in any liquid derivative.

Recent chemical evidence has indicated that disilyl sulphide, $(SiH_3)_2S$, contains a large amount of π-bond character in the Si-S linkage.[3] To test the above hypothesis, the parachor of this substance was measured. The experimental parachor for $(SiH_3)_2S$ was found to be 221·3, and the calculated values, using the atomic parachor for sulphur in organic sulphides[6] were 223·2 (polar Si-H value) and 198·6 (nonpolar Si-H value). Consequently, the hypothesis is valid for disilyl sulphide, since it is necessary to use the polar Si-H bond parachor to obtain agreement with the experimental value.

From this experiment the Si-S bond parachor is found to have a value of 23·4.

[1] A. P. MILLS and C. A. MACKENZIE *J. Amer. Chem. Soc.* **76,** 2672 (1954).
[2] A. I. VOGEL, W. T. CRESSWELL, G. J. JEFFERY, and J. LEICESTER *Chem. and Ind.* 358, (1950).
[3] H. J. EMELÉUS, A. G. MACDIARMID, and A. G. MADDOCK *J. Inorg. Nucl. Chem.* **1,** 194 (1955).
[4] B. J. AYLETT, H. J. EMELÉUS, and A. G. MADDOCK *ibid.* 187, (1955).
[5] F. G. A. STONE and D. SEYFERTH *ibid.* 112 (1955).
[6] A. I. VOGEL *J. Chem. Soc.* 1842, (1948).

EXPERIMENTAL

Apparatus. The surface tension was determined *in vacuo* by a capillary rise method using two capillaries of different diameters.[7, 8] The apparatus was standardized with water and then checked with analytical reagent-grade benzene at 20°C. The average of four readings gave a value for the surface tension of benzene of 28·55 dynes/cm. The literature value at this temperature is 28·89 dynes/cm.[9]

Disilyl Sulphide. This was prepared from silyl iodide and mercuric sulphide.[3] Its purity was checked by measuring its vapour pressure at 0·0°C (found 6·22 cm, calculated[3] 6·08 cm). The density of disilyl sulphide at 18°C was calculated from its density-temperature equation.[3]

RESULTS

The average of four readings gave a value for the surface tension of disilyl sulphide of 22·31 dynes/cm at 18°C. The parachor was calculated from the relationship

$$P = \frac{M\gamma^{1/4}}{d},$$

where P = parachor, M = molecular weight, γ = surface tension, and d = liquid density.

[7] T. W. RICHARDS and E. K. CARVER *J. Amer. Chem. Soc.* **43**, 827, (1921).
[8] H. MILLS and P. L. ROBINSON *J. Chem. Soc.* 1823, (1927).
[9] *Handbook of Chemistry and Physics.* (36th edition.) Chemical Rubber Publishing Company, Cleveland, Ohio (1954), page 1992.

J. Inorg. Nucl. Chem., 1956, Vol. 2, pp. 325 to 329. Pergamon Press Ltd., London

THE SILYL GROUP AS AN ELECTRON ACCEPTOR

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(*Received* 15 *February* 1956)

Abstract—The reaction of silyl iodide with anhydrous hydrazine has been studied, and the compound tetrasilylhydrazine, $N_2(SiH_3)_4$, has been isolated and characterized. It is stable *in vacuo* at 90°, detonates in air, and is a powerful reducing agent. The compound has been found to be monomeric and to form no adducts with silyl iodide or trimethylamine, and these facts are interpreted in terms of "internal compensation" involving the use of dative π-bonds.

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A GOOD deal of evidence has been presented in recent years as to the electron-accepting powers of the SiH_3- or silyl group. In the first place, when silicon is already bound by a σ-bond to another atom, an additional dative bond of the $p_\pi - d_\pi$ type may be formed, utilizing one of the vacant silicon *d*-orbitals. A theoretical discussion of this effect[1] has shown how the effective increase in bond order to a value greater than 1 becomes greater as the electronegativity of the attached atom increases; in addition, some of the chemical consequences have been summarized recently.[2] Where the attached atom is one belonging to Group 5 or 6, normally possessing marked electron-donor properties, these properties will be greatly weakened after attachment to a silyl group. Such an effect has been demonstrated in the case of $N(SiH_3)_3$[3] and $(SiH_3)_2S$,[4] both of which possess very feeble basic character. The removal of *p* electrons for dative π-bond formation also alters the hybridization around the atom concerned, as is evidenced by the planar configuration of $N(SiH_3)_3$[5] and the linear one of $(SiH_3)NCS$[6]—presumably requiring sp^2 and *sp* hybridization respectively.

Secondly, it appears that addition compounds can be formed, using some of the 3*d* orbitals to accommodate electrons from sterically suitable donors.[7] The 1:1 adducts between silyl bromide or iodide and the methylphosphines, described by SUJISHI and WITZ[8] and also the 2:1 compound between trimethylamine and silyl iodide,[2] seem to be compounds of this type; the last has been shown to give a nonconducting solution in acetonitrile. On the other hand, 1:1 adducts between silyl chloride or iodide and, in particular, certain amines have been found to yield conducting solutions in suitable solvents,[2, 9] and it seems likely that these

[1] D. P. CRAIG, A. MACCOLL, R. S. NYHOLM, L. E. ORGEL, and L. E. SUTTON *J. Chem. Soc.* 332 (1954).
[2] B. J. AYLETT, H. J. EMELÉUS, and A. G. MADDOCK *J. Inorg. Nucl. Chem.* **1**, 187 (1955).
[3] A. STOCK and C. SOMIESKI *Ber.* **54B**, 740 (1921).
[4] H. J. EMELÉUS, A. G. MACDIARMID, and A. G. MADDOCK *J. Inorg. Nucl. Chem.* **1**, 195 (1955).
[5] K. HEDBERG and A. J. STOSICK *Abstracts of XIIth International Congress of Pure and Applied Chemistry*, New York, September 1951, p. 543.
[6] A. G. MACDIARMID and A. G. MADDOCK *J. Inorg. Nucl. Chem.* **1**, 411 (1955).
[7] F. G. A. STONE and D. SEYFERTH *J. Inorg. Nucl. Chem.* **1**, 112 (1955).
[8] S. SUJISHI and S. WITZ *J. Amer. Chem. Soc.* **76**, 4631 (1954).
[9] H. J. EMELÉUS and N. MILLER *J. Chem. Soc.* 819 (1939).

compounds are not derivatives of pentacovalent silicon, as has been suggested,[7] but are salt-like in character.[10]

Hydrazine was found to react with excess silyl iodide in the gas phase at room temperature to form tetrasilylhydrazine, $N_2(SiH_3)_4$, together with a white solid of very low volatility, unchanged silyl iodide, and a little hydrogen and monosilane. Yields were never more than about 40%, based on the amount of silyl iodide reacting, and it is suggested that, although the main overall reaction is:

$$5N_2H_4 + 4SiH_3I = N_2(SiH_3)_4 + 4N_2H_5I \quad (1)$$

stepwise substitution probably occurs, and the partially silylated hydrazines react both with hydrazine and with each other to give polymeric Si-N-H compounds with elimination of hydrogen. Disproportionation of these partially silylated derivatives would lead also to production of monosilane. STOCK and SOMIESKI[3] found a similar instability in the silyl derivatives of ammonia, $NH(SiH_3)_2$ and $NH_2(SiH_3)$. This interpretation is favoured by the combining ratio of hydrazine to silyl iodide (1·4–1·5 : 1), which is larger than that given by equation (1).

The tetrasilylhydrazine so formed was a colourless liquid remarkably stable to heating *in vacuo*; a sample maintained at 90°C for 40 min suffered no decomposition, whereas many silyl derivatives decompose rapidly at room temperature. It was, however, explosively oxidized by the air. The Trouton constant was normal, indicating the lack of any large intermolecular attraction. Water reacted with the compound to give hydrogen and a white solid of very low volatility, and it is considered that this may contain Si-O-Si linkages between N-N units. Aqueous alkali, however, caused complete and quantitative breakdown of the compound to hydrogen, salts of silicic acid, and hydrazine, and this fact was used in analysis. As might be expected, the compound acted as a powerful reducing agent,[11] rapidly changing anhydrous copper sulphate to copper, and mercuric chloride to mercurous chloride and mercury.

From the chemical point of view, however, the most interesting effect is the reduction in donor properties of the nitrogen atom. Silyl iodide was chosen as a suitable reference acceptor molecule, since it is known to combine readily, under widely differing conditions, with those nitrogen-containing compounds in which electrons are available for donation.[2] It will not, however, combine with certain compounds, such as trisilylamine and disilylmethylamine, where it is known that the availability of electrons for donation is much lessened or entirely absent.[8, 9, 12] It was shown that even at low temperatures there is little tendency to compound formation between silyl iodide and tetrasilylhydrazine. A small negative deviation from RAOULT's law was the only effect indicated. Thus tetrasilylhydrazine resembles trisilylamine in its greatly lessened basic character. It was possible that the silyl groups would, in addition to forming σ- and dative π-bonds with N atoms in tetrasilylhydrazine, be able to accept further electrons from a suitable donor. To test this possibility, vapour-pressure studies were carried out on tetrasilylhydrazine-trimethylamine mixtures, and the two compounds were sealed together under pressure. Trimethylamine was chosen both because it is an extremely powerful donor, and

[10] C. EABORN *J. Chem. Soc.* 2047 (1955).
[11] cf. L. F. AUDRIETH and B. A. OGG *The Chemistry of Hydrazine*, Wiley, New York pp. 134–7 (1951).
[12] A. B. BURG and E. S. KULJIAN *J. Amer. Chem. Soc.* **72**, 3103 (1950).

because it is known to form adducts with some silyl compounds.[2, 9] No trace of compound formation was found, however.

It appears, then, that tetrasilylhydrazine possesses negligible donor or acceptor properties, and may be regarded as "internally compensated." An indication that such compensation may not be complete, however, is given by the melting-point. A comparison of the physical properties of this compound and of tetramethylhydrazine[13] (Table 1) shows that although the boiling-point and the density of the silicon compound are, as expected, somewhat higher than those of the carbon compound, the melting-point of the former is almost 100°C higher. Such a large difference may well be due to increased intermolecular attraction in the case of tetrasilylhydrazine, although the effects of differing crystal-lattice energies and of possible structural differences cannot be ignored.

TABLE 1

	$N_2(SiH_2)_4$	$N_2(CH_3)_4$
b. pt. °C	109/760 mm	73/730 mm
m. pt. °C	−24	−118
$density_{(20)}$ g/ml	0·83	0·78

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EXPERIMENTAL

The vacuum apparatus and the production of silyl iodide have been described elsewhere.[2] Hydrogen evolved during reaction was measured by means of a Toepler pump; pressures were determined with all-glass spoon gauges. Hydrazine was dried by long standing *in vacuo* over barium oxide and sodium hydroxide,[14] and finally purified by fractional distillation in the vacuum system.

Reaction of silyl iodide with hydrazine. Two bulbs of approximately 50-ml capacity were connected by a 2-litre flask, and the whole attached to the vacuum system. A known weight of silyl iodide was placed in one bulb, and of hydrazine in the other, and the whole sealed off. The two reactants were then allowed to warm up, so that the two vapours met in the flask. A white solid was immediately formed, sometimes of a meringue-like consistency. The volatile products were later removed by means of a diaphragm and magnetic breaker and examined in the vacuum system. A series of such experiments was performed; in a typical one, 2·1216 g of silyl iodide reacted with 0·2811 g of hydrazine for 15 min at room temperature. The products were 55·0 ml of hydrogen, 0·017 g of monosilane (passed through −140°C; M, 33. Calc. for SiH_4, 32), a trace of disilane, 1·133 g of unreacted silyl iodide (held at −96°C, M, 158. Calc. for SiH_3I, 158) and about 50 mg of a substance held at −64°C. This substance was freed from traces of iodine-containing compounds by distilling it *in vacuo* into a small flask containing about 10 g silver powder (<100 mesh, washed with NH_4OH, water, and acetone, and dried *in vacuo*) and allowing it there to warm to room temperature for 1 h. Further purification by repeated fractional condensation at −64° yielded pure tetrasilylhydrazine (Found: M 153, 152, 154; H 7·94, 7·98%; Si 72·8%. Calc. for $N_2(SiH_3)_4$: M 152, H 7·94%, Si 73·7%). Analysis was carried out by hydrolysing a known quantity of the compound with 20% potassium hydroxide solution; hydrazine was shown to be present in the hydrolysate. The ready solubility of the substance in tap-grease made vapour-density determinations difficult; no reaction with the grease appeared to take place, however.

The melting-point was measured in the usual stock apparatus. A specially purified middle

[13] J. B. CLASS, J. G. ASTON, and T. S. OAKWOOD *J. Amer. Chem. Soc.* **75**, 2937 (1953).
[14] Ref. 11, p. 49.

fraction was split into three parts, and the melting-points found to be −24·1°, −24·1°, −24·0°. Vapour-pressure measurements gave the following data:

Temp. °	−22·8	−16·2	−5·9	0·0	5·6	10·6
v. p. (mm)	1·2	2·0	4·2	6·2	9·1	12·3
Temp.°	23·7	31·4	37·6	46·3	52·6	58·8
v. p. (mm)	26·3	39·0	53·9	80·7	107·0	137·8
Temp.°	64·2	68·9	72·8	77·6	82·2	
v. p. (mm)	167·4	200·3	232·0	276·6	325·2	
Temp.°	86·5	90·0				
v. p. (mm)	376·0	421·3				

The extrapolated b. p. was 109·5° ± 0·5°, the latent heat of vaporization 8190 cal/g-mole, and Trouton's constant 21·4. The approximate liquid density was 0·83 g/ml at 20°C.

Reactions of tetrasilylhydrazine. 0·024 g of the substance was sealed in a small glass bulb, and allowed to warm to room temperature. On suddenly breaking the bulb, there was a loud sharp explosion, accompanied by an orange flame. In another experiment, tetrasilylhydrazine (0·0321 g) and air-free water (0·1033 g) were allowed to warm together to room temperature. A white solid was formed, in addition to 8·9 ml hydrogen. Further hydrogen was slowly evolved, and after 24 h no product more volatile than water could be detected. In particular, no $(SiH_3)_2O$ was formed. The final nonvolatile product evolved hydrogen on treatment with alkali, and therefore still contained some Si-H links.

About 0·2 g of anhydrous mercuric chloride was treated with 0·050 g of tetrasilylhydrazine at room temperature. A yellow coloration was immediately produced on the surface of the chloride; this later darkened, and after 10 min was a dark grey colour. On removing all volatile material, 0·032 g tetrasilylhydrazine was recovered, together with a small quantity of mercury vapour (seen to coalesce into droplets under magnification).

About 0·1 g of anhydrous copper sulphate was treated with 0·032 g tetrasilylhydrazine at room temperature. No reaction occurred at first, but after 15 min a reddish-brown coating became noticeable on the powder. After 30 min no tetrasilylhydrazine remained. The remaining solid was with difficulty dissolved in water, and a reddish-brown precipitate of metallic copper isolated.

Donor properties of tetrasilylhydrazine. Tetrasilylhydrazine (0·0594 g) and silyl iodide (0·0622 g; 1:1 mole ratio) were sealed together, and the following vapour-pressure data recorded:

Temp.°	−37·5	−35·3	−34·0	−32·6	−30·7	−28·0
v. p. (mm)	6·8	8·2	8·8	9·7	10·9	13·0
Temp.°	−26·2	−24·2	−21·1	−17·8	−15·4	−12·3
v. p. (mm)	14·2	16·1	19·1	22·6	25·6	29·2
Temp.°	−9·1	−5·4	−2·5	−0·1	3·0	5·8
v. p. (mm)	34·3	40·5	45·1	48·9	54·2	59·0

These values lay on a smooth curve, close to and below that calculated on the basis of RAOULT's law for such a mixture. There was no indication of compound formation.

Acceptor properties of tetrasilylhydrazine. In an initial experiment, tetrasilylhydrazine (0·0473 g) and excess trimethylamine (90·1 ml) were sealed together under pressure. No compound formation was observed, and no evolution of hydrogen or other evidence of reaction occurred. 65·1 ml of the trimethylamine were then removed by fractional distillation, and the resulting tetrasilylhydrazine-trimethylamine mixture (1:3·6 mole ratio) subjected to vapour pressure measurements.

Temp.°	−36	−30	−25	−22	−18	−15	−11	−7·5
v. p. (mm)	126	158	188	204	217	239	289	332
Temp.°	−2	+3	−3	−5·5	−8	−13	−20	−26
v. p. (mm)	399	480	440	381	331	276	215	173
Temp.°	−34	−43	−48					
v. p. (mm)	140	86	69					

These points lay on a smooth curve, with good agreement between readings taken with increasing and decreasing temperatures. Below about −35°, the values correspond to the vapour pressure of

[15] E. SWIFT and H. P. HOCHANADEL *J. Amer. Chem. Soc.* **67**, 880 (1945).

pure trimethylamine;[15] above that temperature, the vapour pressure gradually approaches and becomes slightly less than the value to be expected, on the basis of RAOULT's law, for a mixture containing 78 mole per cent trimethylamine.

In a further experiment, tetrasilylhydrazine (0·0313 g) and trimethylamine (4·09 ml; mole ratio 1: 0·88) were sealed together, and the vapour pressure determined at varying temperatures.

Temp.°	−62	−52	−42	−31	−26	−20	−14
v. p. (mm)	13·7	15·0	18·6	29·7	37·2	47·7	56·5
Temp.°	−7	−1·5	−9	−20	−29	−37	−46
v. p. (mm)	70·9	91·0	69·5	45·5	31·7	24·6	16·6
Temp.°	−56	−65					
v. p. (mm)	14·2	12·5					

The same type of curve was again obtained, but this time the negative deviation from RAOULT's law was greater, and only below −50° did the vapour pressures observed exceed the partial pressure of trimethylamine present. In neither case was any compound formation apparent.

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J. Inorg. Nucl. Chem., 1956, Vol. 2, pp. 330 to 339. Pergamon Press Ltd., London

SOME ASPECTS ON THE CRYSTAL CHEMISTRY OF OXYGEN COMPOUNDS OF MOLYBDENUM AND TUNGSTEN CONTAINING STRUCTURAL ELEMENTS OF ReO_3 OR PEROVSKITE TYPE

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(*Received* 21 *November* 1955)

Abstract—The various types of distortion of the MO_6 octahedra of several molybdenum-oxygen and tungsten-oxygen compounds containing structural elements of ReO_3 or perovskite type may be ascribed to the coexistence of an ionic bonding system with a homopolar bonding system, implying six-, five-, four-, or possibly also three-co-ordination around tungsten and six- and five-co-ordination around molybdenum. Decreasing average valency of the M atom and increasing temperature favour the occurrence of bond systems with high co-ordination number. The differences in the bonding systems of molybdenum and tungsten are probably related to the remarkable structural differences between the oxides of the two metals.

INTRODUCTION

IN the nonmetallic oxides of molybdenum and tungsten, the crystal structures of which are known, the metal atoms are generally surrounded by six oxygen atoms in a more or less distorted octahedral arrangement.[1, 2] Only in the compound Mo_4O_{11} do metal atoms occur with a tetrahedral environment of oxygen atoms, a quarter of the molybdenum atoms being so surrounded, while the remainder show the normal octahedral arrangement of oxygen atoms.[3] Moreover, in the alkali tungsten bronzes (A_xWO_3, $x < 1$), the tungsten and oxygen atoms are arranged to form metal-oxygen octahedra.[2, 4]

In several of the oxygen compounds of molybdenum and tungsten, the metal-oxygen octahedra are coupled together by sharing corners to form an arrangement of *ReO_3 type* extending through the entire structure or part of it. Some tungsten bronzes, e.g. the cubic sodium compound,[5] may be described either as being of ReO_3 type with the alkali atoms randomly distributed in the major interstices of the tungsten-oxygen framework, or as being of *perovskite type* with vacant alkali atom positions. In the following, the various structures or structural elements will be considered as BO_3 structures of ReO_3 type or, which is obviously equivalent, as A_xBO_3 structures ($x \leq 1$) derived from the perovskite type.

During recent years there has been a great interest in the conditions for the formation of structures of perovskite type. The occurrence of polymorphous compounds with differently distorted perovskite structures has attracted considerable attention in connection with the occurrence of ferro-electricity. These problems

[1] A. MAGNÉLI *Nova Acta Regiae Soc. Sci. Upsaliensis* [4] **14**, No. 8 (1950).
[2] G. HÄGG and A. MAGNÉLI *Rev. Pure Appl. Chem.* (*Australia*) **4**, 235 (1954).
[3] A. MAGNÉLI *Acta Chem. Scand.* **2**, 861 (1948).
[4] A. MAGNÉLI and B. BLOMBERG *Acta Chem. Scand.* **5**, 372 (1951).
[5] G. HÄGG *Z. physik. Chemie* (B) **29**, 192 (1935).

have been discussed by MEGAW[6] and many other authors. The following survey will compare the compounds of molybdenum and tungsten containing ReO_3-type structure elements with each other and with other compounds of perovskite type.

CLASSIFICATION OF COMPOUNDS OF MOLYBDENUM AND TUNGSTEN BY THE EXTENSION IN SPACE OF THEIR ReO_3-TYPE STRUCTURE ELEMENTS

It is useful in dealing with the structures of these compounds to classify them in the following groups:

(i) *Structures containing an infinite three-dimensional framework of ReO_3 type.* This group comprises the room-temperature[7, 8] and high-temperature modifications[9] of tungsten trioxide, the cubic sodium[5] and lithium tungsten bronzes,[10, 11] the tetragonal sodium and lithium tungsten bronzes of distorted ("degenerated") perovskite type,[12] and the phases described as "crystalline tungsten blue", H_xWO_3.[13]

The low-temperature modification of tungsten trioxide[14] might also belong to this group. The role of the hydrogen atoms in "crystalline tungsten blue" is not known. However, they are most probably in some way or other associated with oxygen atoms, which might thus as an approximation be considered as hydroxyl groups. The three-dimensional framework of B and O or OH atoms present in all the compounds listed above is evidently analogous to that occurring in all perovskite-type compounds.

(ii) *Structures containing infinite slabs or layers of ReO_3 type.* Structures of this kind showing slabs or layers of various thickness are represented by the molybdenum and molybdenum-tungsten oxides of the homologous series M_nO_{3n-1} ($n = 8$, 9, 10, 11, 12, and 14)[15, 16], the closely related tungsten oxide $W_{20}O_{58}$, the only known member of the series M_nO_{3n-2}, the molybdenum oxide Mo_4O_{11},[3] and the yellow molybdic acid, $MoO_3 \cdot 2H_2O$.[18]

In the oxides of the series M_nO_{3n-1} and M_nO_{3n-2}, the slabs of ReO_3 type are of considerable thickness, n being a measure of their finite extension. Adjacent slabs are orientated parallel to one another and joined by MO_6 octahedra sharing edges.

The layers appearing in Mo_4O_{11} have a thickness corresponding to three MoO_6 octahedra. The orientation of the octahedra of neighbouring layers is not parallel. The layers are mutually connected by MoO_4 tetrahedra.

The yellow molybdic acid is built up of single layers of MoO_6 octahedra joined by corners, the layers of composition (MoO_4^{2-}) probably being kept together by H_4O^{2+} ions.[18] This compound, because of its pronounced salt character, evidently differs considerably from the others treated in this discussion.

[6] H. D. MEGAW *Acta Cryst.* **5**, 739 (1952).
[7] H. BRÄKKEN *Z. Krist.* **78**, 484 (1931).
[8] G. ANDERSSON *Acta Chem. Scand.* **7**, 154 (1953).
[9] W. L. KEHL, R. G. HAY, and D. WAHL *J. appl. Phys.* **23**, 212 (1952).
[10] A. MAGNÉLI and R. NILSSON *Acta Chem. Scand.* **4**, 398 (1950).
[11] M. E. STRAUMANIS and S. S. HSU *J. Amer. Chem. Soc.* **72**, 4027 (1950).
[12] A. MAGNÉLI *Acta Chem. Scand.* **5**, 670 (1951).
[13] O. GLEMSER and C. NAUMANN *Z. anorg. Chemie* **265**, 288 (1951).
[14] B. T. MATTHIAS and E. A. WOOD *Phys. Rev.* **84**, 1255 (1951).
[15] A. MAGNÉLI *Acta Cryst.* **6**, 495 (1953).
[16] A. MAGNÉLI, B. BLOMBERG-HANSSON, L. KIHLBORG, and G. SUNDKVIST *Acta Chem. Scand.* **9**, 1382 (1955).
[17] A. MAGNÉLI *Arkiv Kemi* **1**, 513 (1950).
[18] I. LINDQVIST *Acta Chem. Scand.* **4**, 650 (1950).

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(iii) *Structures containing infinite strings of ReO_3 type.* Structure elements of this type have been found in the tetragonal potassium tungsten bronze[19] and a closely related tetragonal sodium tungsten bronze.[20]

A formal application of the classification principle used above would lead to the incorporation in this group of all structures containing infinite linear rows of MO_6 octahedra joined by corners. It would also add the alkaline earth molybdates and tungstates, $A^{II}MO_6$, containing discrete MO_6 octahedra as a Group iv. The relationship of these atomic arrangements to the ReO_3 type is, however, very distant, and they are disregarded in what follows.

The tungsten oxide $W_{18}O_{49}$ also contains structural elements of ReO_3 type.[21] Owing to the very complicated structure of this compound, it cannot easily be fitted into the scheme applied above.

DISTORTION OF BO_6 OCTAHEDRA IN PEROVSKITE STRUCTURES

The polymorphism shown by perovskite-type compounds, e.g. barium titanate, is attributed by MEGAW[6] to the fact that the geometry of the structure is compatible with ionic as well as homopolar bonding. The radius ratio r_O/r_B would give an octahedral arrangement of the O atoms around the B atom if the packing were purely ionic. However, the structure has also some homopolar character, and the orbitals available for homopolar bonding change with temperature. This brings about sudden small alterations of the geometry of the BO_6 octahedra, leading to phase transitions. The various modifications of barium titanate are illustrated in Fig. 1.

The high-temperature form of barium titanate is cubic, containing regular TiO_6 octahedra. The stable homopolar bonding system in this structure must evidently coincide with the ionic packing. It is thus octahedral for the titanium atom. With decreasing temperature, the symmetry becomes tetragonal. The titanium atom is slightly displaced along one diagonal (four-fold axis) of the octahedron, which is correspondingly distorted towards a square pyramidal arrangement of oxygen atoms around the titanium atom (TiO_5 being the homopolar bonding system) with an additional remote oxygen atom. In the low-temperature modifications (orthorhombic and rhombohedral barium titanate), the titanium atoms are displaced relative to two and three respectively of the diagonal directions of the TiO_6 octahedra, which are distorted in the orthorhombic form towards a tetrahedral TiO_4 arrangement with two additional remote oxygen atoms, and in the rhombohedral form towards pyramidal TiO_3 groups with three remote oxygen atoms completing the octahedra. The homopolar bonding systems are thus TiO_4 tetrahedra and TiO_3 pyramids respectively. With regard to the displacements of the titanium atoms, the TiO_6 octahedra of the various barium titanate modifications may be described as regular and distorted in one, two, or three dimensions.

The titanium atoms are throughout displaced in the same direction in the various noncubic barium titanate forms (parallel distortion). The unit cell contains one formula unit of $BaTiO_3$ for all these phases as well as for the cubic modification.

[19] A. MAGNÉLI *Arkiv Kemi* **1**, 213 (1949).
[20] A. MAGNÉLI *Arkiv Kemi* **1**, 269 (1949).
[21] A. MAGNÉLI *Arkiv Kemi* **1**, 223 (1949).

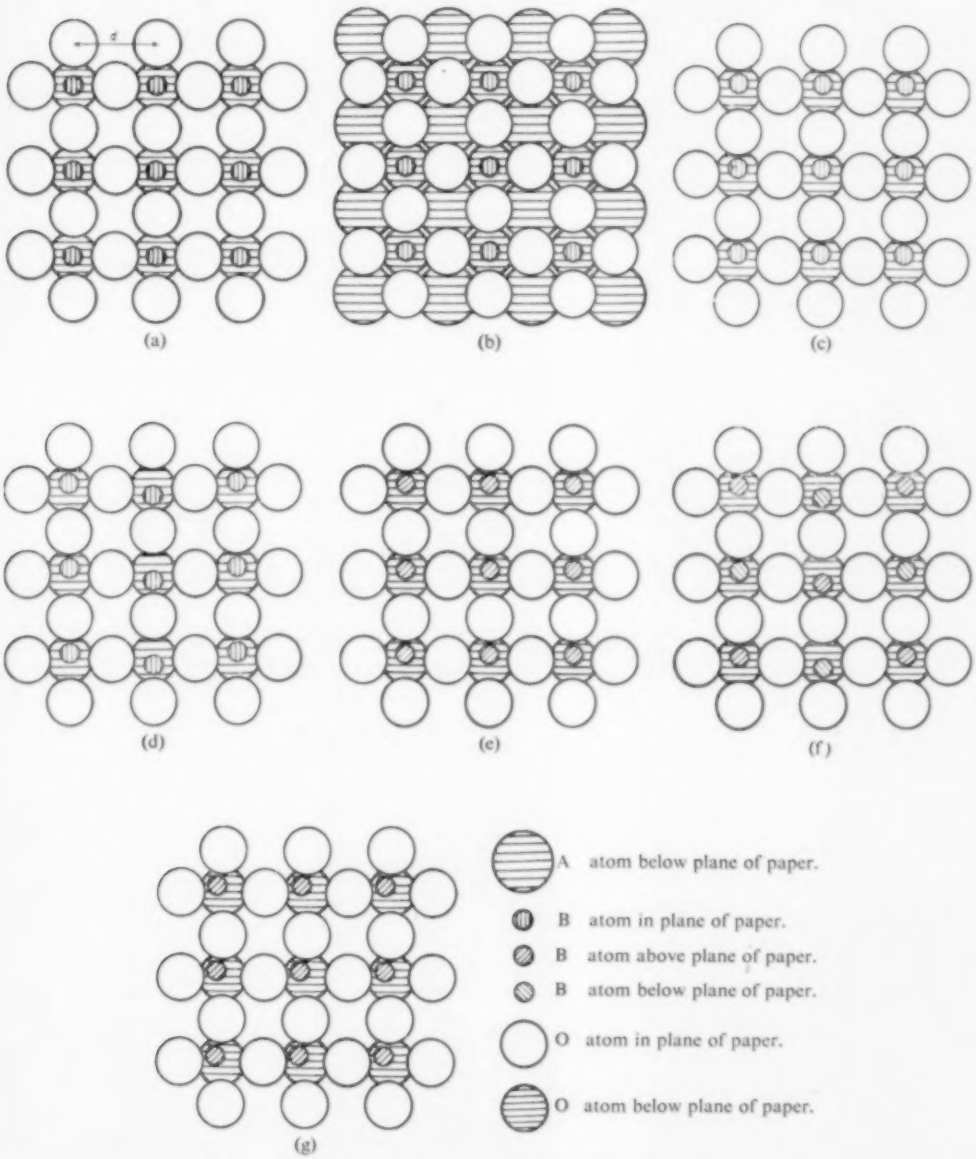

FIG. 1.—Displacement of B atoms in ReO_3-type (BO_3) and perovskite-type (ABO_3) structures. The B atoms are surrounded by six O atoms, the O atom nearest to the reader being omitted to show the underlying atoms. Only the displacements of the B atoms are indicated. The A atoms are omitted except in (b).

(a) Ideal ReO_3-type structure with regular BO_6 octahedra. (b) Ideal perovskite type, e.g. cubic barium titanate. (c) Titanium oxygen framework of tetragonal barium titanate. Parallel displacement of B atoms in one dimension. (d) Structure of tetragonal tungsten trioxide. Antiparallel displacement of B atoms in one dimension. (e) Titanium oxygen framework of orthorhombic barium titanate. Parallel displacement of B atoms in two dimensions. (f) Structure of monoclinic (pseudo-orthorhombic) tungsten trioxide. Antiparallel displacement of B atoms in two dimensions. (g) Titanium oxygen framework of rhombohedral barium titanate. Parallel displacement of B atoms in three dimensions.

However, antiparallel displacements of the B atoms of a perovskite phase ABO_3 might also occur (cf. Fig. 1d), leading to a "puckered structure" and a unit cell comprising two or more formula units of ABO_3 (multiple cell). MEGAW[6] has pointed out the connection between the occurrence of puckered structures and the size of the A atom. If the latter is too small for its site, or if this space is not occupied by an atom, then the formation of a puckered, multiple-cell arrangement is favoured.

CLASSIFICATION OF COMPOUNDS OF MOLYBDENUM AND TUNGSTEN ACCORDING TO TYPE OF DISTORTION OF MO_6 OCTAHEDRA

It is possible to make a tentative classification of these compounds according to the distortion of their MO_6 octahedra. Before doing so, two difficulties must be mentioned.

First, a detailed discussion of the structural features is to some extent obstructed by the inadequate knowledge of the light-atom positions in the complicated structures. Thus the oxygen co-ordinates may be relatively inaccurate for the molybdenum compounds and still more so for the tungsten compounds, where they have generally been derived by arguments based on packing considerations and analogy with known structures. However, the positions of the heavy-metal atoms are known with a fairly high degree of accuracy, and this makes it often possible to deduce the shape of the MO_6 octahedra. (No detailed structure determinations have been carried out for the phases of "crystalline tungsten blue,"[13] and these compounds will not be considered further.)

Secondly, where the regions of ReO_3 or perovskite type are of limited extension, the metal-atom positions do not necessarily reflect the geometry of the metal-oxygen framework as clearly as for those where the regions are wide or infinite. Distortions of the MO_6 octahedra may occur, which are not due to the bonding conditions within the ReO_3- or perovskite-type region, but are caused by the close vicinity of other structural elements. This will apply particularly to structures included in Group iii above, notably the tetragonal potassium tungsten bronze, which will not be discussed further.

The other compounds may be classified as follows:

Regular octahedra. In the isomorphous cubic tungsten bronzes of sodium and lithium (of respective compositions Na_xWO_3 with $0{\cdot}25 < x < 1$, and Li_xWO_3 with $0{\cdot}31 < x < 0{\cdot}57$, the actual limits of composition being dependent on the temperature of formation),[5, 22, 23] the positions of the tungsten and oxygen atoms are given by the symmetry of the lattice. The WO_6 octahedra are evidently regular.

The arrangement of the molybdenum and oxygen atoms within the ReO_3-type slabs of Mo_4O_{11}[3] corresponds to fairly regular MoO_6 octahedra. Likewise the tungsten atoms within the slabs of $W_{20}O_{58}$[17] are regularly distributed according to a simple lattice of nearly cubic symmetry, which makes it highly probable that the WO_6 octahedra of this compound are not significantly distorted. The structure is obviously not puckered, but it corresponds to a multiple of the basic subunit of ReO_3 type. However, owing to the occurrence in $W_{20}O_{58}$ of WO_6 octahedra which share edges,

[22] M. E. STRAUMANIS *J. Amer. Chem. Soc.* **71**, 679 (1949).
[23] B. W. BROWN and E. BANKS *J. Amer. Chem. Soc.* **76**, 963 (1954).

this is not a multiple structure in the same sense as the puckered perovskite-type structures.

One-dimensionally distorted octahedra. In the tetragonal high-temperature modification of tungsten trioxide,[9] neighbouring metal atoms are alternately displaced in opposite directions, parallel to one of the four-fold axes of the basic cubic atomic arrangement. The unit-cell dimensions are $a = d\sqrt{2}$ and c somewhat larger than d (d representing the length of the space diagonal of a regular MO_6 octahedron). This shows that the structure corresponds to the type illustrated in Fig. 1(d), viz. antiparallel one-dimensional distortion.

The same kind of distortion is exhibited by the isomorphous tetragonal sodium and lithium tungsten bronzes (Na_xWO_3, $x \approx 0{\cdot}1$) of distorted perovskite type[12] and by the members of the homologous oxide series $(Mo, W)_nO_{3n-1}$.[16]

The yellow molybdic acid, $H_4O{\cdot}MoO_4$,[18] which has ReO_3-type slabs only one layer thick, shows antiparallel one-dimensional displacements of the metal atoms in the plane of this layer, indicating the existence of a zig-zag arrangement of one-dimensionally distorted MoO_6 octahedra. The corresponding five-co-ordination may, however, be affected by the influence of the H_4O^{2+} ions.

Two-dimensionally distorted octahedra. In the monoclinic room-temperature form of tungsten trioxide[7, 8], the metal atoms show antiparallel displacements along two of the fourfold axes of the basic cubic arrangement. The unit cell comprises four formula units of WO_3. The structure, illustrated in Fig. 1(f), has been described by MEGAW[6] as puckered in two dimensions.

Three-dimensionally distorted octahedra. These have so far not been shown to exist in oxygen compounds of molybdenum and tungsten. However, it may be that this type of distortion is present in the low-temperature modification of tungsten trioxide.[14]

CONDITIONS FOR THE OCCURRENCE OF THE VARIOUS TYPES OF MO_6 DISTORTION

Fig. 2(a) illustrates the temperature dependence of the structure of barium titanate, the modifications with three-, two-, and one-dimensionally distorted octahedra and regular octahedra successively appearing with increasing temperature. Such a sequence of modifications has been found, more or less complete, for a considerable number of perovskite-type compounds,[6] and it seems reasonable to assume that the phase transitions are due to similar distortions of the BO_6 octahedra. The sequence is similar for tungsten trioxide (cf. Fig. 2b). A modification with undistorted WO_6 octahedra has, however, not been observed for this substance. As mentioned above, the structure of the low-temperature modification may correspond to a three-dimensionally distorted arrangement, but, so far, this hypothesis has not been tested experimentally.

The character of the distortion of the MO_6 octahedra in molybdenum and tungsten compounds is represented in Fig. 3(a), (b) as a function of the average valency of the M atom. For the molybdenum compounds, the diagram refers to a temperature of about 750°C, i.e. close to the stability region of all three phases indicated.[16] The data for the tungsten compounds are likely to be pertinent up to the transition temperature of monoclinic to tetragonal tungsten trioxide. These diagrams show a striking similarity to those given in Fig. 2, increasing temperature and decreasing

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valency thus changing the character of the octahedra in an analogous way. The valency of the M atom evidently provides a means for correlating the compounds containing infinite and finite structural units of ReO_3 type. Of course this does not imply that the valency and temperature are the only fundamental quantities determining the structural details.

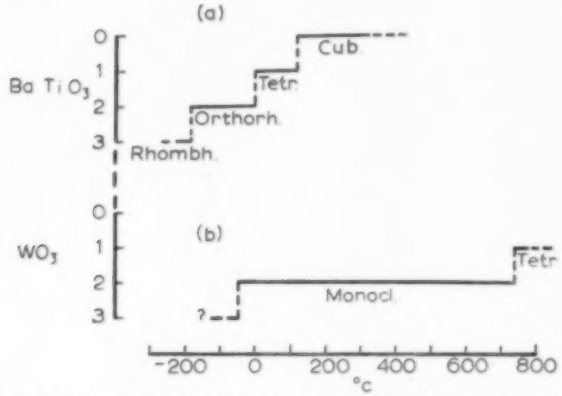

FIG. 2.—Type of distortion of BO_6 octahedra vs. temperature. Symbol $n = 0$, 1, 2, and 3 represents regular octahedra and octahedra distorted in one, two, and three dimensions respectively. (a) Barium titanate. (b) Tungsten trioxide.

The combined effect of temperature and valency on the type of distortion of the MO_6 octahedra is demonstrated by the molybdenum oxides of the homologous series M_nO_{3n-1}. Of these, Mo_8O_{23}, corresponding to an average valency of molybdenum of 5·75, is obtained at about 700°C, while Mo_9O_{26} (valency 5·78) forms at about 750°C. Increase of valency evidently requires increase of temperature in order to obtain the conditions necessary for the formation of oxide phases with the same kind of MO_6 distortion. This suggests that phases of other homologous series which may exist in the molybdenum and tungsten oxygen systems are likely to appear at progressively higher temperatures as the extension of the ReO_3-type slab increases.

It is obvious that the various types of distortion of the MO_6 octahedra occur within restricted intervals of valency of the M atoms. The appearance of the diagram Fig. 3(b) for the tungsten compounds suggests that an oxide (or possibly a series of oxides) might exist of composition between WO_3 and $WO_{2\cdot90}$ built up of one-dimensionally distorted WO_6 octahedra. Such an oxide would have a very complicated formula and structure and, although it might be built on simple structural principles somewhat like those of the M_nO_{3n-1} or M_nO_{3n-2} series, it should give complicated X-ray diagrams very similar to those of tungsten trioxide. Some indications have in fact been found of the possible existence of a phase, α'-tungsten oxide, of composition very close to WO_3 and giving powder photographs extremely similar to those of the trioxide.[24]

From Fig. 3(a) and (b) it is obvious that there is a remarkable disparity between the valency differences associated with a change of the distortion type for molybdenum and tungsten. Thus the covalent bonding system of the latter proceeds from four- to five-co-ordination and from five- to six-co-ordination when the valency changes

[24] G. HÄGG and A. MAGNÉLI *Arkiv Kemi, Mineral. Geol.* **19A**, No. 2 (1944).

from 6 to 5·9 and from 5·9 to 5·8 respectively. For molybdenum the transition from five- to six-co-ordination corresponds to a change of valency of about 0·25. This suggests that the differences of energy between the various states of co-ordination are larger for molybdenum than for tungsten, which may be relevant to the fact that no molybdenum compounds have been found containing two-dimensionally distorted MoO_6 octahedra.

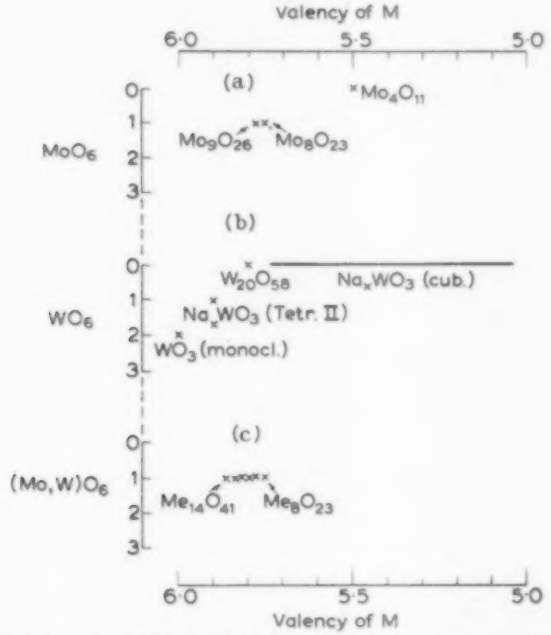

FIG. 3.—Type of distortion of BO_6 octahedra vs. average valency of B. (a) MoO_6 octahedra. (b) WO_6 octahedra. (c) $(Mo,W)O_6$ octahedra.

While tungsten is thus readily adaptable to six-, five-, four-, and possibly also to three-co-ordination, molybdenum seems to have a preference to enter into five-co-ordination by directing five of the six oxygen atoms surrounding it towards a square pyramidal arrangement. This conclusion is supported by the observations that molybdenum is able to replace tungsten only to a very limited extent in tungsten trioxide[25, 26] and not at all in the cubic sodium tungsten bronze.[27] On the other hand, tungsten can partially replace molybdenum in Mo_9O_{26} and, in addition, higher tungsten contents encourage the formation of higher homologues within the series M_nO_{3n-1}.[16] The increase in the relative content of tungsten evidently means that the conditions for the occurrence of one-dimensionally distorted MO_6 octahedra are reached at a higher average valency of the metal atoms (cf. Fig. 3c).

It was pointed out above that the molybdenum atoms of the yellow molybdic acid, $MoO_3 \cdot 2H_3O$, are likely to have a square pyramidal arrangement of oxygen atoms as closest neighbours. Also, in molybdenum trioxide[7, 28, 29] the structure of

[25] A. MAGNÉLI *Acta Chem. Scand.* **3**, 88 (1949).
[26] A. MAGNÉLI and S. WESTMAN, To be published.
[27] M. E. STRAUMANIS and K. K. IRANI *J. Amer. Chem. Soc.* **74**, 2114 (1952).
[28] N. WOOSTER *Z. Krist.* **80**, 504 (1931).
[29] G. ANDERSSON and A. MAGNÉLI *Acta Chem. Scand.* **4**, 793 (1950).

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which is not related to the ReO_3 type, the metal atoms tend towards five-co-ordination, being surrounded by octahedra distorted to a square pyramid.

In the homologous series of molybdenum and molybdenum-tungsten oxides M_nO_{3n-1}[16] showing one-dimensional distortion of the MO_6 octahedra, the degree of distortion may be measured by the length of the b axis of the various preparations. Fig. 4 illustrates how the ratio $b:d$ varies with the relative content of tungsten (x),

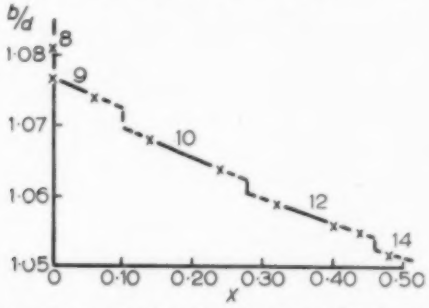

FIG. 4.—Ratio b/d vs. tungsten content in oxides of composition $(Mo_{1-x}W_x)_nO_{3n-1}$, where b is the distance between opposite corners of the actual MO_6 octahedron in the direction of distortion and d (assumed to be 3·75 Å) that between opposite corners of an undistorted MO_6 octahedron. The figures 8–14 correspond to the values of n.

where d is the distance in a regular octahedron between opposite corners, assumed to be 3·75 Å. The different values for the pure molybdenum oxides and the discontinuities in the curve (which are real, and not within the limits of experimental error of the observations) show that the thickness of the ReO_3-type slabs affects the degree of distortion of the octahedra. However, it is also obvious that increasing content of tungsten reduces the distortion for each single phase. It is thus reasonable to assume either that different bonding orbitals are engaged in the five-co-ordination of the two metals or that the fraction of ionic bonding is higher for tungsten than for molybdenum. The latter assumption is possibly supported by the fact that the number of s electrons is higher for tungsten than for molybdenum, the ground states being $5d^46s^2$ and $4d^55s^1$ respectively.

The distortion of the MO_6 octahedra of the molybdenum-oxygen and tungsten-oxygen compounds is antiparallel throughout. This is in agreement with the idea put forward by MEGAW[6] that, when A atoms are too small for their sites in ABO_3 perovskite structures or when the A-atom positions are vacant, this will favour the formation of puckered structures.

CONCLUSIONS

The main conclusions from the discussion presented above are as follows:

I. The distortions of the MO_6 octahedra present in several molybdenum oxides, tungsten oxides, and alkali tungsten bronzes containing structural elements of ReO_3 or perovskite type are analogous to those of BO_6 octahedra in the polymorphic forms of several structures (ABO_3) of perovskite type.

II. The occurrence of regular MO_6 octahedra and various types of distorted MO_6 octahedra may, following MEGAW,[6] be ascribed to the co-existence of an ionic bonding system with a homopolar bonding system implying six-, five-, four-, or possibly also three-co-ordination around the M atom.

III. The occurrence of the various types of MO_6 octahedra is connected with the average valency of the M atom and with the temperature. The valency presents a means of systematically arranging and comparing compounds with infinite and finite structural elements of ReO_3 or perovskite type. Decreasing valency and increasing temperature favour the occurrence of bond systems with higher co-ordination number.

IV. While tungsten is easily adaptable to a homopolar bonding system of six-, five-, four-, and possibly also three-co-ordination, considerably higher energy barriers separate these bonding systems for molybdenum, which shows a preference for five-co-ordination.

V. The degree of distortion of one-dimensionally distorted WO_6 octahedra is considerably less than for MoO_6 octahedra. This suggests either that the homopolar bonding system for five-co-ordination corresponds to different orbitals for the two metals, or that the fraction of ionic bonding is higher for tungsten than for molybdenum.

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VI. The differences of the bonding systems of molybdenum and tungsten mentioned in the two preceding paragraphs are probably related to the remarkable structural differences between the oxides of the two metals, the dioxides being the only instance of isomorphism, and possibly also to the nonexistence of molybdenum bronzes.

Acknowledgements—These studies form part of a research programme on metal oxides and related compounds financially supported by the Swedish Natural Science Research Council.

J. Inorg. Nucl. Chem., 1956, Vol. 2, pp. 340 to 344. Pergamon Press Ltd., London

VIBRATIONAL ASSIGNMENTS FOR METAL AMMINES

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(*Received* 1 *February* 1956)

Abstract—The infra-red spectra of a number of di-, tetra-, and hexammine metal complexes have been measured as solids in KBr wafers. The spectra are analysed in terms of known assignments for similar methyl compounds, and a generalized assignment is obtained for the metal-ammine complexes. The assigned frequency region for a given type of vibration appears generally to be quite insensitive to the co-ordination number and the nature of the metal.

PROBLEMS of structure and bond type in inorganic co-ordination compounds can now, with the use of KBr techniques for obtaining infra-red spectra of solids, be conveniently studied by means of infra-red spectra. Successful application of this approach requires a basic schematic assignment of the vibrational modes of the types of co-ordination compounds to the absorptions in the various regions of the spectra. The present work provides such a basic assignment of the absorption bands of some metal-ammine complexes.

Some vibrational spectra of metal-ammine complexes have been published. HILL and ROSENBERG[1] and FAUST and QUAGLIANO[2] have reported on the absorption bands of a number of cobalt (III) complexes and have discussed the possible vibrational assignments of some of these absorptions. MERRITT and WIBERLEY[3] have considered the assignment of the 6- and 12-μ bands of some ammonia and ethylene diammine complexes of cobalt (III), and KOBAYASHI and FUJITA[4] have reported the spectra of the hexammine complexes of nickel, chromium, and cobalt. Raman spectra of a number of inorganic complexes have been obtained[5] and provide some help in assigning the infra-red bands.

EXPERIMENTAL

The metal-ammine complexes were all prepared by standard procedures described in the literature.[6] These purified compounds were analysed for nitrogen by treatment with excess alkali, to liberate the ammonia which was collected in a solution of standard acid. The excess acid was then determined by titration with standard base and the amount of ammonia was calculated. Chloride analyses were also made by the gravimetric method of weighing the precipitated silver chloride. In every case the analysis found was in good agreement with the calculated value.

ANDERSON, SPOOR, and BRISCOE[7] have shown, using heavy water, that the hydrogens in metal ammines readily exchange with the solvent hydrogens. Therefore the technique employed for the synthesis of the deuterated ammines was to allow the light complex to stand in deuterium oxide. Approximately 10 mg of the metal ammine was placed in a small glass tube containing 1 ml of D_2O and the stoppered tube was allowed to stand overnight at room temperature. Its contents were then

[1] D. G. HILL and A. F. ROSENBERG *J. Chem. Phys.* **22,** 148 (1954).
[2] J. P. FAUST and J. V. QUAGLIANO *J. Amer. Chem. Soc.* **76,** 5346 (1954).
[3] P. E. MERRITT and S. E. WIBERLEY *J. Phys. Chem.* **59,** 55 (1955).
[4] M. KOBAYASHI and J. FUJITA *J. Chem. Phys.* **23,** 1354 (1955).
[5] JEAN-PAUL MATHIEU *J. Chim. Phys.* **36,** 308 (1939).
[6] J. N. FRIEND *A Text Book of Inorganic Chemistry—Metal Ammines* Charles Griffin and Co. Ltd., London, 1928, Vol. 10, Chapters IV and V.
[7] J. S. ANDERSON, N. L. SPOOR, and H. V. A. BRISCOE *J. Chem. Soc.* 361 (1943).

frozen by surrounding the tube with a dry ice-acetone bath, and it was then attached to a vacuum line. The system was evacuated and the water removed from the sample by condensing it in an adjacent tube surrounded by a dry ice-acetone bath. A second 1-ml portion of D_2O was then added to the solid metal ammine in the reaction tube and the entire procedure repeated. The final solid product is believed to be primarily the desired deuterated ammine.

Spectra were obtained in the rock-salt region, 4000 to 650 cm^{-1}, on a Baird Associates instrument. A superimposed polystyrene spectrum served as calibration. For lower frequencies, down to about 300 cm^{-1}, a Perkin-Elmer Model 112 instrument with CsBr optics was used. Atmospheric water-vapour bands then provided the calibration. Some typical spectra are reproduced in Fig. 1 and discussed in detail below.

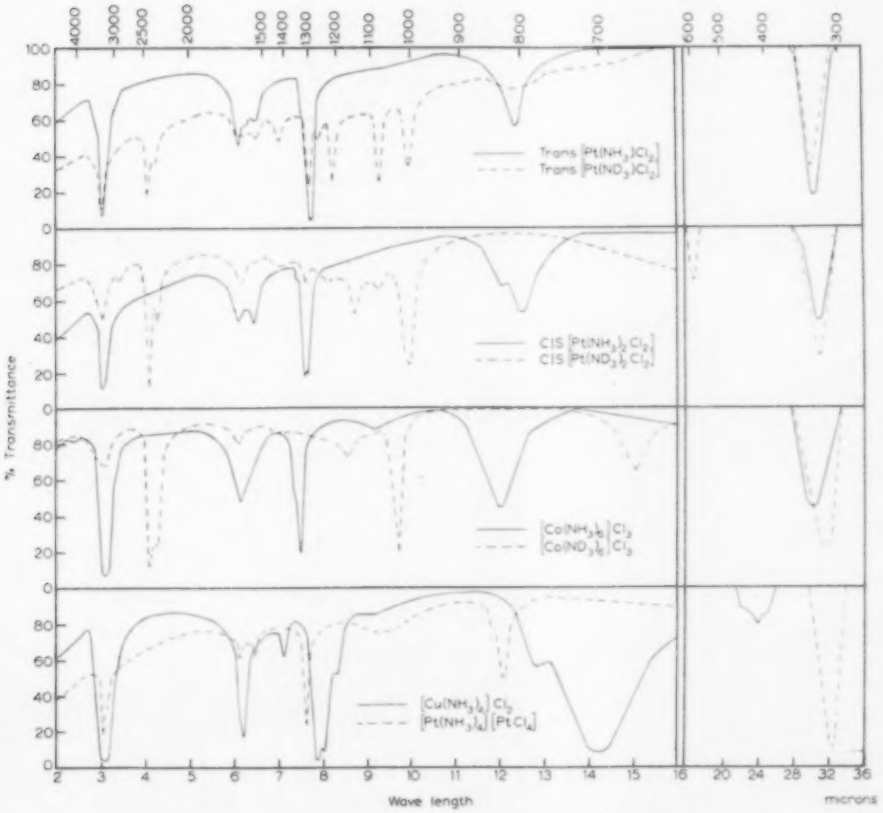

FIG. 1.—Infra-red spectrum of some metal ammines in KBr.

RESULTS AND DISCUSSION

The more intense bands of some linear diammines arranged along with the assigned infra-red active bands of ethane are shown in Table 1. In addition to ammine bands analogous to the CH_3 absorptions in ethane, there will be an antisymmetric metal-nitrogen stretching and, at frequencies probably lower than are reached, a

N-M-N bending mode. Table 2 presents similar results for the bent diammines arranged along with the absorption bands, descriptions, and notation for the bands of propane, excepting the methylene-group vibrations. In both types of diammine the correlation of the N-H stretching and bending modes with the corresponding C-H vibrations is an adequate basis for the assignment given in the tables. Further, the general splitting of the bent diammine bands is expected on the basis of the lower symmetry.

TABLE 1.—INFRA-RED ABSORPTION BANDS AND ASSIGNMENTS FOR SOME LINEAR DIAMMINES

Ethane			*Ammines*			
Description	Sym-metry	Fre-quency (cm^{-1})	$Pt(NH_3)_2Cl_2$	*trans*-$Pt(NH_3)_2Cl_4$	$[Ag(NH_3)_2]_2SO_4$	$Cu(NH_3)_2Cl_2$
C-H stretching, ν_7	E'	2994	3320	3080	3360	3340
C-H stretching, ν_3	A_2''	2954				3250
CH_3 deformation, ν_8	E'	1486	1632	1550	1646	1608
					1600	
CH_3 deformation, ν_6	A_2''	1379	1288	1342	—*	1252
CH_3 rocking, ν_9	E'	821	806	934	732	711
				(550)		633
				(505)	(600)	481
			326	300		306

* Obscured by the sulphate absorption.

Only for the band assigned as an NH_3 rocking mode is there a possible confusion with the skeletal stretching mode, which might be expected, however, at some still lower frequency. To distinguish these assignments, the spectra of some deuterated ammines were studied. Table 3 shows the bands of the deuterated platinum ammines that can be correlated with the parent ammine. Since the deuterium exchange was not complete, a number of additional bands, not listed in Table 3, showed up as the partially deuterated analogues. It is clear, however, that all the frequencies for the *cis*- and *trans*-$Pt(NH_3)_2Cl_2$ above the lowest observed frequencies of 322 and 328 cm^{-1} shift by a factor of about 1·3 on deuteration. It follows then that in these compounds the absorptions at about 800 cm^{-1} are to be assigned to the NH_3 rocking mode, while the skeletal stretching motion gives rise to the bands at about 320 cm^{-1}. On the basis of this interpretation, the bands of the other diammines might be assigned. The additional bands of some of these ammines, however, do not permit any satisfactory schematic assignment to be supplied in this region.

A guide to the assignment of the tetrammines are those given for the tetramethyl compounds of lead, tin, and germanium reported by LIPPINCOTT and TOBIN.[8] Table 4 gives the more intense bands of several tetrammines arranged with the descriptions and frequency ranges of the tetramethyl compounds. Again, as with the diammines, a fairly good direct correlation can be made, the only ambiguous region being that between 400 and 800 cm^{-1}. Assignment of the lower-frequency band, below 400 cm^{-1}, to the skeletal stretching mode and that at about 800 cm^{-1} to the rocking motion can

[8] E. R. LIPPINCOTT and M. C. TOBIN *J. Amer. Chem. Soc.* **75**, 4141 (1953).

probably be made on the basis of the deutero experiments with the diammines and the hexammine reported below.

As an example of a hexammine, the spectra of $Co(NH_3)_6Cl_3$ and $Co(ND_3)_6Cl_3$ are given in Table 5. For octahedral symmetry and an assumed free rotation of the NH_3 groups, molecular symmetry O_h, the expected infra-red active absorption bands, symmetry class f_{1u}, are listed together with the corresponding descriptions.

TABLE 2.—INFRA-RED ABSORPTION BANDS AND ASSIGNMENTS FOR SOME BENT DIAMMINES

Propane			*Ammines*			
Description	Symmetry	Frequency (cm^{-1})	*cis*-$Pt(NH_3)_2Cl_2$	$Hg(NH_3)_2Cl_2$	$Zn(NH_3)_2Cl_2$	$Cd(NH_3)_2Cl_2$
C-H stretching,						
ν_{18}, ν_{12}	B_2, B_1	2968			3380	3360
ν_1	A_1	2960	3290	3150	3290	3260
ν_{13}, ν_2	B_1, A_1	2885				
CH_2 deformation,						
ν_{19}, ν_3	B_2, A_1	1470	1626	1614	1604	1605
ν_{14}	B_1	1465	1546	1411	1401	1408*
CH_3 deformation,						
ν_{15}	B_1	1375	1309	1263	1257	1207
ν_4	A_1	1370	1299		1241	
CH_3 rocking,						
ν_5, ν_{21}	A_1, B_2	1152	826			
ν_{16}	B_1	1053	796	714	665	556
ν_{20}	B_2	748				
C-C stretching,						
ν_{17}	B_1	922	322	471	422	374
ν_6	A_1	870			306	

* Present as a weak band in $Cd(NH_3)_2Br$.

TABLE 3.—SPECTRA OF DEUTERATED DIAMMINES (FREQUENCIES IN CM^{-1})

trans-$Pt(NH_3)_2Cl_2$	*trans*-$Pt(ND_3)_2Cl_2$	*cis*-$Pt(NH_3)_2Cl_2$	*cis*-$Pt(ND_3)_2Cl$
3220 (s)	2450 (s)	3290 (s)	2450 (s)
1632 (s)	1213 (s)	1626 (s)	1150 (m)
		1546 (m)	1083 (w)
1288 (s)	1003 (s)	1309 (s)	1008 (s)
		1299 (s)	
806 (s)	—*	826 (m)	594 (w)
		796 (s)	
326 (s)	332 (s)	322 (s)	322 (s)

* No absorption in the region around 600 cm^{-1} was observed. The spectrum of the deutero complex, however, shows only a very weak absorption, corresponding to the undeuterated component, at 800 cm^{-1}.

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TABLE 4.—SPECTRA AND ASSIGNMENTS FOR SOME TETRAMMINES

Description	Symmetry	Frequency	$Pt(NH_3)_4Cl_2.H_2O$	$Zn(NH_3)_4I_2$	$Cu(NH_3)_4Cl_2$	$Cd(NH_3)_4Cl_2$	$Hg(NH_3)_4(ClO_4)_2$
CH stretching, ν_{13}	F_2	3000	3200	3290	3270	3360	3420
ν_{11}		2920				3260	3320
CH_3 deformation, ν_{15}	F_2	1440	1587	1600	1596	1608	—*
CH_3 deformation, ν_{16}	F_2	1200	1340	1242	1245	1207	1244
			1326				
CH_3			880				691
rocking, ν_{17}	F_2	800	842	693	709	561	611
M-C stretching, ν_{18}	F_2	480-600	497	410	420	381	408

* Obscured by presence of a perchlorate band at 1611 cm^{-1}.

TABLE 5.—INFRA-RED SPECTRA AND ASSIGNMENTS FOR THE COBALT HEXAMMINES

Description	$Co(NH_3)_6Cl_3$	$Co(ND_3)_6Cl_3$
N-H stretching	3205 (s)	2430 (s)
N-H stretching		
N-H bending, sym.	1619 (m)	1161 (w)
N-H bending, antisym.	1327 (s)	1021 (s)
N-H rocking	828 (s)	663 (m)
Co-N stretching	330 (s, b)	310 (b)

SUMMARY

The ammine groups in metal-ammine complexes have characteristic absorption regions only slightly dependent on the metal ion and on the number of ammine groups attached. These differences, while probably important in determining the details of the bonding in these compounds,[9] are not usually sufficient to disturb the assignment to a type of deformation of the group. Only in the low-frequency range of the NH_3 rocking and M-N stretching frequencies is there, as might be expected, much sensitivity to the nature of the compound. One can, however, expect for any metal-ammine complex absorptions attributable to the N-H stretching (3200–3300 cm^{-1}), the antisymmetric NH_3 deformation (1600 cm^{-1}), the symmetric NH_3 deformation (1200–1340 cm^{-1}), the NH_3 rocking mode (600–900 cm^{-1}), and the M-N stretching mode (300–500 cm^{-1}). The assignment of KOBAYASHI and FUJITA[4] of the absorptions of the hexammines of nickel(II), chromium(II), and cobalt(III) at 682, 762, and 830 respectively to a M-N stretching mode does not agree with our assigned regions and, in particular, the hexamminecobalt (III) absorption at 830 cm^{-1} has been shown here by the deuterium experiments to be, in fact, a predominantly hydrogen motion.

[9] D. N. SEN., S. MIZUSHIMA, C. CURRAN, and J. V. QUAGLIANO *J. Amer. Chem. Soc.* **77**, 211 (1955).

J. Inorg. Nucl. Chem., 1956, Vol. 2, pp. 345 to 347. Pergamon Press Ltd., London

THE CRYSTAL STRUCTURE OF ANTIMONY TRICHLORIDE

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(*Received* 23 *January* 1956)

Abstract—The crystal structure of antimony trichloride, $SbCl_3$, has been determined. The dimensions of the orthorhombic unit cell are $a = 6{\cdot}37$ Å, $b = 8{\cdot}12$ Å, and $c = 9{\cdot}47$ Å. The space group is *Pbnm*.

The following parameters have been obtained:

4Sb in 4(*c*) with $x = 0{\cdot}025$ and $y = 0{\cdot}992$
$4Cl_I$ in 4(*c*) with $x = 0{\cdot}667$ and $y = 0{\cdot}075$
$8Cl_{II}$ in 8(*d*) with $x = 0{\cdot}133$ and $y = 0{\cdot}183$ and $z = 0{\cdot}067$.

In the antimony trichloride molecules, which form the crystal structure, the distance Sb–Cl is $2{\cdot}36 \pm 0{\cdot}03$ Å and the angle Cl–Sb–Cl $95{\cdot}2°$.

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1. INTRODUCTION

THIS work is part of an investigation of ionizing solvents. The problems which we intend to study have been discussed in an earlier paper[1] dealing with the constitution of arsenic trichloride solutions. The crystal structure of arsenic trichloride has not been studied as yet, because of difficulties in preparing single crystals at low temperatures. Antimony trichloride has, however, the same solvent properties and can be studied at room temperature. The main principles of the two structures may be expected to be similar.

2. EXPERIMENTAL

Crystals

$SbCl_3$ crystals are very hygroscopic. A single crystal was therefore grown in a thin capillary (0·1 mm thick) by a method of successive melting and crystallization. (Another modification can be obtained from a solution in carbon disulphide.[2])

X-ray Investigation

Weissenberg photographs were taken, with Mo*K* radiation, around the capillary direction. This was shown by precession photographs to coincide with a face-diagonal [011] of the orthorhombic single crystal grown in the capillary. Fourteen layers were obtained.

The cell dimensions are $a = 6{\cdot}37$ Å, $b = 8{\cdot}12$ Å, and $c = 9{\cdot}47$ Å. The density given by GROTH[2] corresponds to 4 (3·96) $SbCl_3$ in this unit cell.

The conditions for possible reflections were found to be $k = 2n$ for $0kl$ and $h + l = 2n$ for $h0l$. The probable spacegroups are $Pbn2_1$ (No. 33) or *Pbnm* (No. 62).

The intensities were estimated visually. Each reflection hkl occurred in two Weissenberg photographs because of the rotation around [011]. A good correlation between the different layers was obtained in this way. The results indicate an accuracy of 15–20% for the intensity estimation.

Relative $|F|^2$ values were calculated from the estimated intensities, using LU's curves.[3]

The absorption can be calculated in this case, but a rough calculation shows that the variation is within 20%. The procedure used for the intensity estimation also partially corrects the absorption, and no further correction was made.

3. STRUCTURE DETERMINATION

The three-dimensional Patterson function, $P(x,y,z)$, was calculated on the Hägg-Laurent machine.[4] The parameters of the Sb and Cl positions could then be deduced in a rather straightforward way.

[1] I. LINDQVIST *Acta Chem. Scand.* **9**, 73 (1955).
[2] P. GROTH *Chem. Kryst.* (*Leipzig*) **I**, 227. (1906).
[3] CHIA-SI LU *Rev. Sci. Instrum.* **14**, 331 (1943).
[4] G. HÄGG and T. LAURENT *J. Sci. Instrum.* **23**, 155 (1946).

The Patterson function could be interpreted in terms of either *Pbnm* or $Pbn2_1$. If $Pbn2_1$ was adopted, the values of the parameters derived implied the higher symmetry *Pbnm*. The structure is thus best described with the most symmetrical space-group *Pbnm*.

The parameters arrived at were:

4Sb in 4(*c*) with $x = 0{\cdot}025$ and $y = 0{\cdot}992$
$4Cl_I$ in 4(*c*) with $x = 0{\cdot}667$ and $y = 0{\cdot}075$
$8Cl_{II}$ in 8(*d*) with $x = 0{\cdot}133$ and $y = 0{\cdot}183$ and $z = 0{\cdot}067$

These positions would give rise to the following maxima in $P(x,y,z)$:

3Sb—Sb maxima in (0·050, 0·016, 0·500)
(0·500, 0·484, 0·500)
(0·450, 0·500, 0·000)
$4Sb—Cl_I$ maxima in (0·358, 0·083, 0·000)
(0·308, 0·068, 0·500)
(0·142, 0·432, 0·500)
(0·182, 0·417, 0·000)
$4Sb—Cl_{II}$ maxima in (0·108, 0·191, 0·183)
(0·158, 0·175, 0·317)
(0·392, 0·325, 0·317)
(0·342, 0·309, 0·183)

Maxima very near these points were obtained in $P(x,y,z)$. No other maxima of the same magnitude were found.

The atomic positions were confirmed by calculation of three electron-density projections which showed no unexplained maxima higher than about one-quarter of the heights of the chlorine maxima. Finally, three sections of the three-dimensional electron density function $\rho(x,y,z)$ were calculated in order to obtain best possible parameters. The section $\rho(x,y,\frac{1}{4})$ gave the accurate parameters for Sb and Cl_I. $\rho(x,y,0{\cdot}067)$ gave the x,y parameters and $\rho(0{\cdot}125,y,z)$ the y,z parameters for Cl_{II}.

The results finally obtained were:

Sb : $x = 0{\cdot}025$, $y = 0{\cdot}995$
Cl_I : $x = 0{\cdot}671$, $y = 0{\cdot}077$
Cl_{II} : $x = 0{\cdot}132$, $y = 0{\cdot}176$ (in both sections), $z = 0{\cdot}066$

The ratio of the heights of the Sb and Cl maxima was of the order of magnitude of 3, which is the ratio between the atomic numbers.

Finally, the structure factors were calculated and an apparent temperature factor $B = 2{\cdot}5$ (which may include some absorption effects) was determined. The R value obtained for all $|F(hkl)|$ measured was 0·13, which is satisfactory.

4. DISCUSSION OF THE STRUCTURE

The structure is shown in Fig. 1.

The most interesting result from our point of view is the fact that there are discrete $SbCl_3$ molecules in the crystal. The dimensions of such molecules are Sb—Cl 2·36 Å (Sb—Cl_I = 2·35 Å and Sb—Cl_{II} = 2·37 Å), Cl—Cl 3·49 Å (3·48 Å and 3·51 Å), and the angle Cl—Sb—Cl 95·2°. The standard deviation calculated for the distance Sb—Cl is ±0·03 Å. These values may be compared with the following data for the molecules in the gas phase, obtained by electron diffraction:[5] Sb—Cl 2·37 ± 0·02 Å,

[5] P. W. ALLEN and L. E. SUTTON *Acta Cryst.* **3**, 46 (1950).

Cl—Sb—Cl 96° ± 4° (SWINGLE, recent investigation) or 104° ± 2° (GREGG *et al.*, 1937). The agreement with SWINGLE's result is excellent.

There are no details in the packing of the molecules which indicate any particularly strong interaction. The Sb—Cl distances between different molecules are long, the

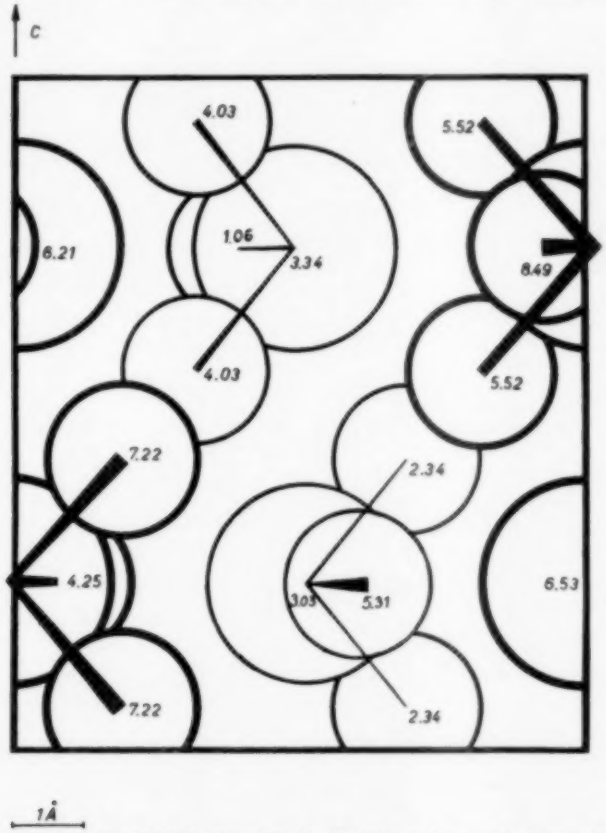

FIG. 1.—The unit cell of $SbCl_3$ viewed in the direction of the *a* axis. Small circles Cl, large circles Sb. The *x* values of the atoms are given in Å.

shortest being 3·5 Å. The solid $SbCl_3$ evidently contains the same molecules as the gas phase. The problem is now to explain the properties of liquid $SbCl_3$, which behaves as an ionizing solvent[6] and is described as "associated."[7] It would be mere speculation, however, to discuss this problem without any further information. First of all, the crystal structures of solvates must be studied, because they constitute the first step in the formation of an electrolytic solution in an ionizing solvent. Such work is in progress in this institute.

Acknowledgements—We are indebted to Mr. LARS HENRIK ANDERSSON for his preparation of the single crystal used. The work was supported by the Swedish Natural Science Research Council, which support is gratefully acknowledged. Finally, we want to thank Professor G. HÄGG for all the facilities put at our disposal.

[6] Z. KLEMENSIEWICZ *Z. phys. Chem.* **A113**, 28 (1924).
[7] P. WALDEN *Molekulargrössen von Elektrolyten*, p. 77. Dresden, 1923.

J. Inorg. Nucl. Chem., 1956, Vol. 2, pp. 348 to 357. Pergamon Press Ltd., London

PERCHLORYL FLUORIDE, ClO_3F

PREPARATION AND SOME PHYSICAL AND CHEMICAL PROPERTIES*

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(*Received* 22 *December* 1955)

Abstract—Perchloryl fluoride ClO_3F has been prepared by electrolysis of a solution of sodium perchlorate in anhydrous hydrogen fluoride, and by reaction of potassium chlorate with elemental fluorine. Some physical constants have been determined and some chemical reactions investigated. Perchloryl fluoride is a colourless gas with a sweet odour. On cooling, it forms a colourless liquid which solidifies at −146°C to a white crystalline solid. The equation for the vapour-pressure curve was determined to be $\log_{10} P_{mm} = 7{\cdot}683–1083{\cdot}8/T$. A boiling-point of −47·5°C was calculated. The gas is quite inert, and has been found to react with only a few substances. Perchloryl fluoride oxidizes potassium iodide solution to give iodine and chloride and fluoride ions. With anhydrous ammonia, two liquid phases are formed and a slow reaction takes place with the formation of a mixture of ammonium fluoride and an ammonium salt of the amide of perchloric acid, $NH_4{\cdot}NH{\cdot}ClO_3$. This ammonium salt forms a stable aqueous solution from which the slightly soluble silver or barium salts of the amide can be precipitated. These salts are explosive, white crystalline solids.

INTRODUCTION

THE extreme electronegativity of fluorine and oxygen permit combination with elements in their highest oxidation states. Many ternary compounds, e.g. oxyfluorides, are relatively volatile, and can be considered the molecular analogues of the oxyanions of the elements in the same oxidation states. Table 1 gives a list of some of these oxyfluorides and fluorides, together with the corresponding oxyanions for two periods of the periodic table of elements.

If the thermal stabilities of these compounds as listed in Table 1 are compared, a decrease toward the right side is found in both periods. In the first period, sulphuryl fluoride, for example, though stable up to several hundred degrees, is of lower stability than is silicon tetrafluoride. Permanganyl fluoride, in the other period, is so unstable that explosive decomposition is likely to occur above 0°C.[1] On the other hand, if the compounds in the two periods are compared for their stability towards hydrolysis sulphuryl fluoride is found to have surprising inertness, whereas the opposite effect is exhibited in the other period, where permanganyl fluoride is again the most reactive compound.

Consideration of the above properties, namely the high stability of sulphuryl fluoride, and the existence of the fluoride of the very unstable permanganic acid, MnO_3F, first suggested the possibility of the existence and preparation of the fluoride of perchloric acid, ClO_3F.

* A joint contribution.
† Presented in part before the Fluorine Symposium of the Ind. Eng. Div., 126th Meeting, A.C.S. New York, September, 12-17 1954. See Abstracts pp. 52 M.
‡ Present address: Chemical Institute, University of Innsbruck, Austria.
[1] A. ENGELBRECHT and A. V. GROSSE *J. Amer. Chem. Soc.* **76**, 2042-45 (1954).

One possible method of preparation and some physical constants of the fluoride of perchloric acid, ClO_3F, were reported in a preliminary publication[2]. The unique chemical and thermal stability of this compound stimulated a more thorough and precise study of its physical constants and chemical reactions.

The electrolysis of fluosulphonic acid in anhydrous hydrogen fluoride yields substantial amounts of sulphuryl fluoride,[3] indicating this electrolysis to be a

TABLE 1.—OXYFLUORIDES, FLUORIDES, AND OXYANIONS OF SOME ELEMENTS IN THEIR HIGHEST OXIDATION STATES

	SiF_4	POF_3	SO_2F_2	ClO_3F	TiF_4	VOF_3	CrO_2F_2[4]	MnO_3F[1]
M.p., °C	−90·2	−39·4	−120	−146	—	300	31·6	−38
B.p., °C	−95·7 subl.	−39·8 subl.	−52	−47·5	284 subl.	480	29·6 subl.	60
Oxyanion	SiO_4^{4-}	PO_4^{3-}	SO_4^{2-}	ClO_4^-	TiO_4^{4-}	VO_4^{3-}	CrO_4^{2-}	MnO_4^-

All the oxyfluorides and fluorides listed in Table 1 are of the general formula: XO_nF_{4-n}, where X is Si, P, Cl, etc. Each of the compounds has a more or less symmetrical, tetrahedral structure.

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successful method for substituting a strongly acidic hydroxyl group by fluorine. Accordingly, the first method used for preparation of perchloryl fluoride was the electrolysis of a saturated solution of sodium perchlorate in anhydrous hydrogen fluoride. The sodium salt was chosen because both the perchlorate and the fluoride are very soluble, forming a highly conductive solution. On application of a voltage of 4–7 V, perchloryl fluoride, ClO_3F, is evolved at the nickel anode together with large quantities of oxygen difluoride and small amounts of oxygen and chlorine. Hydrogen is formed on the iron cathode. Purification of perchloryl fluoride is best achieved chemically, by bubbling the anode gases through sodium hydroxide solution containing a reducing agent, such as sodium thiosulphate. All the higher boiling impurities are thus removed. The purified perchloryl fluoride is condensed in a trap cooled in liquid oxygen.

The electrochemical method of preparation, though practical, has several disadvantages. The current efficiency for electrolysis of sodium perchlorate and HF to perchloryl fluoride is only 10% ClO_3F per faraday, according to $ClO_4^- + HF + H^+ \xrightarrow{2F} ClO_3F + H_2 + \frac{1}{2}O_2$. A more efficient method for preparing perchloryl fluoride was searched for, and was found in the fluorination of potassium chlorate with elemental fluorine. BODE and KLESPER[5] first investigated this reaction. They corrected some of their originally reported results in a recent publication.[6] The new data are in essential agreement with those found by one of the authors of this paper.[7] In the present work several compounds were identified as products of the fluorination of potassium chlorate at temperatures not greatly exceeding 100°C. The relative amounts of these compounds are dependent on the conditions of the reaction, such as temperature, amount of dilution of fluorine with an inert gas,

[2] A. ENGELBRECHT and H. ATZWANGER *Monatsh.* **83**, 1087 (1952).
[3] H. SCHMIDT and H. D. SCHMIDT *Z. anorg. Chem.* **279**, 289 (1955).
[4] A. ENGELBRECHT and A. V. GROSSE *J. Amer. Chem. Soc.* **74**, 5262 (1952).
[5] H. BODE and E. KLESPER *Z. anorg. Chem.* **266**, 275 (1951).
[6] H. BODE and E. KLESPER *Z. angew. Chem.* **66**, 605 (1954).
[7] A. ENGELBRECHT *Z. angew. Chem.* **66**, 442 (1954).

and contact time. The volatile products are, in approximate order of their amounts: ClO_3F, Cl_2, ClO_2F[9], O_2, Cl_2O_6 and ClF. Our tentative interpretation of the mechanism of this reaction is shown in Fig. 1.

At higher temperatures the decomposition of the intermediate (ClO_3) becomes substantial, and relatively more chloryl fluoride and chlorine (and oxygen) are formed. The yields of Cl_2O_6 are particularly sensitive to changes in conditions of the reaction. This is easily understood in the light of a very recent publication by A. J. ARVIA and co-workers,[8] who report their findings about the fluorination

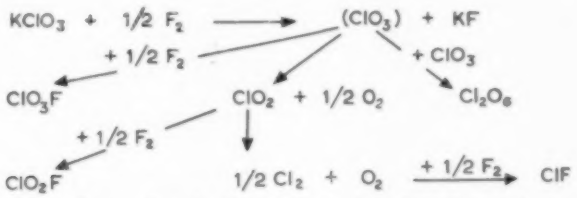

FIG. 1.—Proposed mechanism of fluorination of potassium chlorate.

of Cl_2O_6 with elemental fluorine. According to this publication, and in agreement with our own experiments, Cl_2O_6 reacts very readily with fluorine to yield a mixture of several compounds: ClO_2F, Cl_2O_7, O_2, Cl_2, and others. Preparation of perchloryl fluoride by this reaction gave up to 45% conversion of the fluorine, according to the equation:

$$KClO_3 + F_2 = ClO_3F + KF. \quad (1)$$

Here again the best and safest means of purification was found to be to pass the gases directly through a reducing alkaline solution, condensing the purified perchloryl fluoride in a cold trap.

When chlorine trifluoride is used instead of fluorine, a higher temperature is required to initiate the reaction, and accordingly very little ClO_3F is formed. Main products in this case are ClO_2F and chlorine. Similar results are obtained with liquid bromine trifluoride and potassium chlorate, a reaction which has already been reported as probably yielding ClO_2F.[9] In our work we did not find any perchloryl in the reaction products. No reaction was observed between antimony pentafluoride and potassium chlorate in an experiment made at room temperature.

Pure perchloryl fluoride is a colourless gas with a characteristic sweetish odour.

TABLE 2.—PHYSICAL CONSTANTS OF PERCHLORYL FLUORIDE

Molecular weight	102·45
Melting-point	−146°C ± 2°C
Boiling-point	−47·5°C ± 0·5°C
Vapour pressure	$\text{Log}_{10} P_{mm} = 7{\cdot}683 - 1083{\cdot}8/T$ (−112 to −44°C)
Heat of vaporization	4960 cal/mole
Entropy change by vaporization	21·97
Liquid density	$d = 2{\cdot}455 - 0{\cdot}00329{\cdot}T$ (−110 to −40°C) g/cm³
Critical temperature	95·9°C
Critical density	0·637 g/cm³
Critical molar volume	161 cm³

[8] A. J. ARVIA, W. H. BASUALDO, and J. H. SCHUMACHER *Z. angew. Chem.* **67**, 616 (1955).
[9] A. A. WOOLF *Chem. and Ind.* **12**, 346 (1954).

It is only moderately toxic, as revealed by animal tests carried out at the Jefferson Medical College of Philadelphia.[10] Table 2 summarizes some physical constants of perchloryl fluoride.

Perchloryl fluoride is thermally rather stable, and has never been found to explode even when heated in a tube up to the softening point of glass. It will, however, support combustion as readily as pure oxygen.

Chemically, perchloryl fluoride is distinguished by its inertness. Only two reactions have been found to proceed quantitatively at room temperature within several hours. These involve reactions with potassium iodide solution and with gaseous ammonia.

Perchloryl fluoride will oxidize potassium iodide solutions to give iodine and chloride and fluoride ions. The speed of this reaction increases greatly with increasing acidity of the solution. Four to five hours shaking of a mixture in 0·1 N mineral acids at room temperature will quantitatively reduce the molecule according to the equation:

$$ClO_3F + 8I^- + 6H^+ = Cl^- + F^- + 4I_2^- + 3H_2O \qquad (2)$$

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In presence of sodium bicarbonate this reaction is so slow that it is barely detectable. In stronger alkaline solutions only a very slow hydrolysis to perchlorate and fluoride ions takes place.

The second reaction which proceeds at room temperature, although again only very slowly, is the reaction with gaseous ammonia. When the dry gases, ClO_3F and NH_3, are condensed together, two liquid layers are formed and the slow formation of a white solid can be observed. Repeated vaporization and condensation will speed up the ultimately quantitative reaction, whereby one mole of perchloryl fluoride reacts with three moles of ammonia, as follows:

$$ClO_3F + 3NH_3 = NH_4F + ClO_3NH{\cdot}NH_4(I) \qquad (3)$$

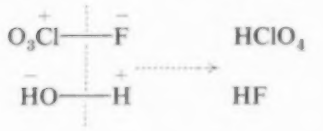
The authors did not succeed in separating this mixture directly, but were able to convert the compound (I) into a silver salt, $ClO_3NH{\cdot}Ag$(II) which is very slightly soluble in water and therefore can easily be freed from ammonium fluoride. The salt-like character of the two compounds, (I) and (II), is analogous to the acidic amides; sulphamide, trisulphamide, and pyrosulphamide,[11] all of which form sparingly soluble silver salts. As was expected, all derivatives of the amide of perchloric acid are highly explosive and must be handled with extreme care, for even the slightest impact may cause a violent explosion. Despite this instability of the dry salts, aqueous solutions or suspensions are sufficiently stable to permit their safe handling. The silver salt can be recrystallized from boiling water without appreciable decomposition. Addition of strong alkali does not seem to decompose the anion $(ClO_3NH)^-$. However, acids will cause decomposition, especially when concentrated or warm. Although the authors have no definite proof, they believe hydroxylamine to be an intermediate in the acid decomposition, assuming a redox

[10] Probable LD_{50} 2000–4000 p.p.m. (4 hours' exposure). This value characterizes the degree of hazard as "moderate, grade 7-8." C. P. Carpenter, H. F. Smyth, jr., and U. C. Pozzani *J. Indust. Hyg. Toxicol.* **31**, 343-346 (1949).

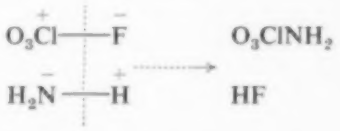
[11] E. Hayek, A. Engelbrecht, and F. Wagner *Monatsh.* **83**, 939 (1952).

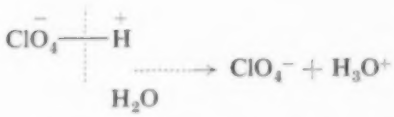
reaction immediately following the formation of the unstable amide, $ClO_3 \cdot NH_2$. A corresponding scheme of reactions would be

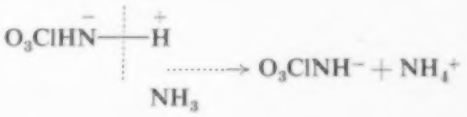
Hydrolysis



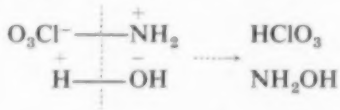
Ammonolysis







Addition of strong acids to the solutions of salts of the amide of perchloric acid will cause the anion O_3ClNH^- to combine with H_3O^+ ions to yield the undissociated amide, O_3ClNH_2. However, this is only of limited stability. It decomposes, whereupon the ClO_3 group proves to be the more electronegative part, and the originally negative NH_2 group is oxidized to NH_2^+, and combines with water to form hydroxylamine.



(If bound to fluorine, the ClO_3 group is of course the more positive part, as indicated by the products of the hydrolysis and ammonolysis of perchloryl fluoride.) While it was easy to show the formation of chloric acid, the authors could not establish the presence of hydroxylamine. This was probably due to secondary reactions between hydroxylamine and the simultaneously formed chloric acid.

The general degree of inertness of perchloryl fluoride is shown by the fact that quantitative hydrolysis to perchlorate and fluoride ions can only be accomplished with concentrated sodium hydroxide solution, by heating to 250° to 300°C in a closed tube. Pure water under similar conditions has very little effect on the compound. The reactions of perchloryl fluoride with sodium or potassium metal, although rather vigorous when started, require temperatures up to 300°C for initiation.

A comparison with the other two known compounds of chlorine, oxygen and fluorine, namely ClO_2F and $ClO_3 \cdot OF$ (both of which are extremely reactive), emphasizes the exceptional characteristics of perchloryl fluoride (Table 3).

TABLE 3.—CHLORINE OXYFLUORIDES

	ClO_2F	ClO_3F	$ClO_3 \cdot OF$[12]
M.p.	−115	−146	−167
B.p.	−6	−47·5	−16
Chemical properties	Reactive	Stable, inert	Explosive, reactive

[12] G. H. CADY and G. H. ROHRBACK *J. Amer. Chem. Soc.* **69**, 677 (1947).

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EXPERIMENTAL

Electrolytic preparation of ClO_3F. The apparatus consisted of a cylindrical iron pot with about 2-l. capacity, surrounded by a cooling jacket. The Teflon insulated nickel anodes were suspended from the cover, while the cell body served as cathode. The parts of the system which were exposed to corrosive fluorides were constructed of standard copper tubing or inert plastic materials (Kel-F, Teflon).

The combined gases from both electrodes, after being stripped of HF in a dry-ice reflux condenser, were bubbled through a solution containing about 10% NaOH and 5% $Na_2S_2O_3$. To avoid plugging, the inlet tube was immersed in trichloroethylene, which formed an inert lower layer in the gas-washing bottle (glass). After a second washing with the same solution, the almost pure ClO_3F was dried with NaOH pellets and condensed in a trap cooled in liquid oxygen. The noncondensible O_2 and H_2 were vented through a sulphuric-acid bubbler. Great care was taken to avoid any material of construction that would react with F_2O and thereby initiate explosion of the gas mixture. Only copper, glass, Kel-F, and Teflon were used, and the rubber stoppers were heavily coated with Fluorolube.

A typical cell charge was 1000 g of anhydrous HF plus 800 g of $NaClO_4$. The solubility of $NaClO_4$ in anhydrous HF had been roughly determined at 20°C to be 95 g $NaClO_4$ in 100 g HF. Operating temperature was from 0° to 30°C applied voltage 5-8 V, which produced a current of 15-20 A. A polarization curve indicated a decomposition potential of around 4·7 V.

The large amounts of by-products, F_2O, O_2, and a little Cl_2 from the anode, and H_2 from the cathode, swept the ClO_3F through the dry-ice condenser. The presence of a reducing compound in the washing solution was necessary to absorb completely the F_2O.

Fluorination of $KClO_3$. The apparatus was designed to give good temperature control for the conversion of the reactants into ClO_3F. As already indicated, high temperatures yielded more ClO_2F and Cl_2, while low temperatures permitted the F_2 to pass through unreacted. Two upright iron pipes were used as reactors. The first one, charged with a mixture of 400 g of dry crystalline $KClO_3$ (BAKER, analysed reagent) and 1400 g of copper shot (for uniform heat transfer), was kept around room temperature. The second reactor was filled with 700 g of crystalline $KClO_3$, and kept between 50° and 60°C. A measured stream of fluorine, varying from 0·2 to 0·5 l./min diluted about 1 : 1 with nitrogen, was introduced at the lower end of Reactor No. 1. The progress of the reaction could be observed by several thermocouples arranged inside the reactor, since the strongly exothermic reaction created a warm zone, which slowly moved upward. Overheating (above 50°C) was avoided by increasing the flow of N_2 or by external cooling. The second reactor served to assure complete reaction of the fluorine. The separation and purification of ClO_3F was accomplished chemically, as in the electrolytic preparation. The effluent gases (ClO_3F, Cl_2, ClO_2F, Cl_2O_6, ClF, O_2, N_2) were passed through several gas-washing bottles filled with a solution of about 10% NaOH and 5% $Na_2S_2O_3$. The first flask again contained a lower layer of trichloroethylene which prevented plugging or too violent reaction on first contact of the gas mixture with the solution. The remaining gases, ClO_3F, O_2, and N_2, were passed through a tower of NaOH pellets and the ClO_3F condensed in a trap refrigerated in liquid oxygen. The end of the gas train was again vented through a H_2SO_4 bubbler to the atmosphere. The whole apparatus was provided with several liquid safety-seals.

Final purification. The practically pure ClO_3F, either from the electrolytic preparation or from fluorination of $KClO_3$, was repeatedly passed through the above-mentioned solution of NaOH and $Na_2S_2O_3$ and dried over NaOH pellets and P_2O_5. The gas densities obtained agreed with the theoretical values.

The infra-red spectrum of ClO_3F. For the purpose of identification and qualitative purity control, the infra-red absorption spectrum of ClO_3F was recorded. To assure highest possible purity, the sample was obtained as the middle fraction of 250 g of repurified ClO_3F. Fig. 2 shows the spectra for three pressures (760, 20, 2 mm Hg at 25°C). A model 21 Perkin-Elmer double-beam spectrophotometer with 100-mm cell length was used in this determination.

Melting-point of ClO_3F. The melting-point of ClO_3F was determined in a cell of the type described by BOOTH and MARTIN.[17] A copper constantan thermocouple (calibrated against the ice point,

[13] A. JAVAN and A. V. GROOSE *Phys. Rev.* **87**, 227 (1952).
[14] A. JAVAN, G. SILVEY, C. H. TOWNES, and A. V. GROSSE *ibid.* **91**, 222 (1953).
[15] A. JAVAN and A. ENGELBRECHT *ibid.* **96**, 649 (1954).
[16] J. F. LOTSPEICH and A. ENGELBRECHT unpublished.

solid CO_2 and boiling O_2) was employed for the determination of the temperature. The warming and cooling curves were identical within the limits of accuracy of temperature determination. The melting-point of ClO_3F under its own vapour pressure was found to be -146 ± 2°C. Perchloryl fluoride solidifies to a crystalline white substance. The very small change of temperature during melting (less than 0·1°C for an 8-g sample) was an indication of the high purity of the material.

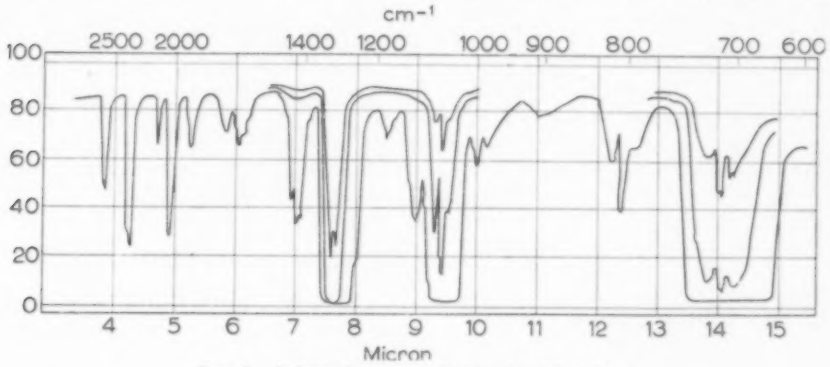

FIG. 2.—Infra-red spectrum of perchloryl fluoride.

Vapour pressure, boiling-point, and gas density of ClO_3F. Determination of the vapour pressure of ClO_3F in the temperature range from $-112°$ to $-44°$C was carried out by the static method. The ClO_3F was contained in the previously mentioned melting-point cell. This cell was immersed in a low-temperature thermostat. The vapour pressure corresponding to the temperature of the sample was recorded on an absolute manometer. The temperature of the ClO_3F sample was found as described in the preceding paragraph. Table 4 gives the vapour pressures at temperatures up to $-43·7°$C. The straight line that resulted from plotting $1/T$ against $\log_{10} P_{mm}$ can be expressed by the equation $\log_{10} P_{mm} = 7·683 - 1083·8/T$. The last column of Table 4 gives the differences between

TABLE 4.—VAPOUR PRESSURE OF PERCHLORYL FLUORIDE

Temp. °C	P_{mm}		Deviation (mm) obsd.-calc.
	Obsd.	Calc.	
−112·0	8·5	9·1	+0·6
−97·2	32	33·5	+1·5
−85·7	81	80·0	−1·0
−77·2	143	142·2	−0·8
−68·0	249	252·3	+3·3
−62·0	355	355·6	+0·6
−58·3	432	436·5	+4·5
−55·7	495·5	501·2	+5·7
−53·0	577	576·8	−0·2
−50·05	651	668·3	+17·3
−48·8	706	714·5	+8·5
−48·0	750	743·0	−7·0
−47·2	784	770·9	−13
−46·6	803	794·3	−8·7
−45·2	855	849·2	−5·8
−43·7	906	914·1	+8·1

[17] H. S. BOOTH and D. R. MARTIN, *J. Amer. Chem. Soc.* **64**, 2198 (1942).

observed vapour pressures and those calculated by use of the equation. Although agreement is not altogether satisfactory, it is believed by the authors that the more or less symmetrical deviations from the calculated values (due to variations in the thermostat) will not greatly influence the results.

The boiling-point of ClO_3F was calculated to be $-47{\cdot}5 \pm 0{\cdot}5$°C at a pressure of 760 mm mercury. The heat of vaporization at the boiling-point is 4960 cal/mole. The change of entropy upon vaporization at $-47{\cdot}5$°C is 21·97 cal/deg. The gas density of ClO_3F was found to be 102·5 g per 22·4 l. at NTP, as calculated for the monomeric molecule.

The liquid density of ClO_3F. A glass pycnometer equipped with a calibrated capillary and a stopcock was used. Ether served as liquid for the low-temperature bath. The temperature was determined as described for the determination of the melting-point. After correction for the cubic expansion coefficient of the glass, and for the ClO_3F in the gas phase, the liquid density between -110 to -40°C was shown to obey the linear equation $d\,.\,(g/cm^3) = 2{\cdot}455 - 0{\cdot}00329T$.

Orthobaric densities, critical constants of ClO_3F. The sealed-tube method of Lowry and Erikson[18] was employed for these measurements. The temperature of meniscus disappearance was recorded as the critical temperature. The critical density was derived by application of the law of rectilinear diameters, and was found to be 0·637 g/cm³ at the critical temperature of 95·9°C.

No experimental determination of the critical pressure was made. The orthobaric densities are given in Table 5.

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Table 5.—Orthobaric densities of perchloryl fluoride

Temp. °C	d/g/cm³	
	Liquid	Vapour
−79	1·84	0·00078
0·0	1·53	0·0326
26·4	1·42	0·0627
41·3	1·35	0·1033
48·2	1·31	0·1109
54·0	1·27	0·128
60·6	1·23	0·1498
70·3	1·16	0·193
75·0	1·125	0·2175
81·4	1·06	0·262
85·0	1·02	0·292
89·8	0·946	0·3486
92·9	0·873	0·4096

The accuracy of the measurements of liquid and vapour densities is believed to be within ±5 and ±12% respectively.

Hydrolysis of ClO_3F. A sample of about 0·3 g ClO_3F was sealed in a pressure-glass tubing together with 1 cm³ water, and heated to 250° C for twelve hours. When the specimen had cooled to room temperature, and the tube was opened, the presence of unreacted ClO_3F was easily detected by its odour. The water contained only a trace of fluoride ions. The same procedure was repeated with a small test tube containing about 2 g of solid NaOH placed inside the pressure tube. Water and ClO_3F were added as before. Upon digestion, quantitative reaction to $NaClO_4$ and NaF was observed. No other products, such as NaCl or $NaClO_3$, were detected.

The reaction of ClO_3F with solid NaOH was extremely slow at room temperature and not very fast with molten NaOH.

Analysis of ClO_3F. The above-described reaction of ClO_3F with water and NaOH at 300°C in a sealed tube was used to analyse for the fluorine and chlorine content. Before analysing, it was found necessary to remove large amounts of $SiO_2{\cdot}xH_2O$ (from reaction of NaOH with the glass

[18] H. H. Lowry and W. R. Erikson *J. Amer. Chem. Soc.* **49**, 2729 (1927).

tube). This was done by shaking the diluted aqueous solution of the reaction products with freshly precipitated cadmium hydroxide. The fluoride ion was determined gravimetrically as CaF_2. The perchlorate ion was reduced with aluminium turnings in presence of $TiOSO_4$, and the resulting chloride ion titrated potentiometrically with silver-nitrate solution. Analysis: calcd. for ClO_3F–F 18·54, Cl 34·61, found—F 18·8, Cl 34·6.

A second set of data on the composition of ClO_3F was provided by reducing the gas with molten metallic sodium or potassium in a quartz tube. As already mentioned, this reaction required heating above 300°C for initiation, but was rather vigorous and was accompanied by a flame. It was found best to heat the metal first in a vacuum while pumping off all evolved gases, and then to introduce the ClO_3F slowly. If no immediate reaction took place, it was preferable to raise the temperature rather than increase the pressure of ClO_3F. This technique prevented sudden ignition and breakage of the tube. When the reaction was complete, the excess metal was removed by reaction with alcohol. Here again it was necessary to remove the $SiO_2{\cdot}xH_2O$ with a suspension of $Cd(OH)_2$. The fluoride was determined potentiometrically with $FeCl_2$. The chloride was titrated by the Mohr method. Analysis: calcd. for ClO_3F—F 18·54, Cl 34·61; found—F 18·6, Cl 34·5.

The oxidation state of chlorine in ClO_3F was proven to be 7 by the quantitative reaction with acidic potassium iodide solution. An excess of strongly acidic (about 1 N HCl or H_2SO_4) KI solution was drawn into a gas density-bulb, which contained a weighed amount of ClO_3F (about 0·3 g). The ClO_3F was reduced according to equation (2). Warming from the outside accelerated the reaction, which required several hours for completion. The liberated iodine was titrated with 0·1 N $Na_2S_2O_3$ solution. Analysis: calcd. for ClO_3F—8 equiv. iodine; found—7·93 equiv. iodine.

Perchloryl fluoride and ammonia. Two liquid layers were formed when ClO_3F was condensed together with dry NH_3 in a trap cooled in dry ice. The compounds combined slowly to give a white nonvolatile solid. This reaction appeared to proceed mainly in the gas phase, and several hours were required for quantitative reaction of a few grams of ClO_3F. The fact that 5·5 g ClO_3F yielded 8·2 g of this solid indicates that one part of ClO_3F had reacted with exactly three parts of NH_3. Qualitative tests proved the fluorine to be present as NH_4F. Attempts to separate the NH_4F from the solid by use of organic solvents were not successful. A quantitative determination of the chlorine content of the mixture (NH_4F + (I)) was carried out by potentiometric titration of the chloride resulting from the reduction of the molecule with aluminium turnings and H_2SO_4 in presence of $TiOSO_4$. The amount of NH_3 given off by boiling the mixture with NaOH solution was also determined. Analysis: calcd. for equi-molecular mixture NH_4F + $ClO_3NH{\cdot}NH_4$—Cl 23·1, N 27·4; found—Cl 23·2, N 18·2. This shows that only two-thirds of the nitrogen was given off as NH_3, and the third nitrogen atom is bound differently.

The silver salt of the amide of perchloric acid. Addition of silver ions to the aqueous solution of the above-described mixture of NH_4F + (I) precipitated a white crystalline, slightly soluble, and light-sensitive compound $ClO_3NH{\cdot}Ag$(II). The solubility in water was determined to be about 1 g in 100 cm³. Acids and ammonia dissolved the compound very readily.

This silver salt, when dried, was extremely explosive, and detonated upon the slightest impact, leaving behind a trace of metallic silver. When stored under water, the compound was stable. It was recrystallized from boiling water, though the temperature coefficient of its solubility was rather small.

The analysis of this silver salt was difficult, mainly because of the stability of the ClO_3NH^- ion in alkaline solution and complex redox reactions upon acid decompositions. The nitrogen content was determined by refluxing the silver salt with an excess of hydrochloric-acid solution of KI, removing the liberated iodine, and distilling the NH_3 from an alkaline solution. Addition of NaOH directly to the silver salt did not liberate any NH_3. The chlorine was determined by dissolving the silver salt in diluted HNO_3, and adding $AgNO_3$ and $NaNO_2$. The resulting AgCl was determined gravimetrically. The silver in the silver salt was precipitated as AgI and weighed as such. Analysis: calcd. for $ClO_3NH{\cdot}Ag$—N 6·78, Cl 17·18, Ag 52·27; found—N 5·73, Cl 15·1, Ag 52·57. The discrepancies in the nitrogen and chlorine values are explained by the unusual procedures required for this analysis.

The barium salt of the amide of perchloric acid. Addition of barium ions to the solution of the silver salt(II) in NH_4OH resulted in a very fine, crystalline, white precipitate. This barium salt was so insoluble that a saturated aqueous solution gave with H_2SO_4 only an opalescence. The dry compound was also explosive, although distinctly less sensitive than the silver salt. It was soluble in

acids and oxidized iodide to iodine in acidic solutions. While the quantitative analysis for the Ba, N, and Cl content established a ratio of these elements very near to 1:1:1, it was not possible to assign a definite formula to this compound.

Acknowledgements—This work was carried out in two sections. The electrochemical preparation, some physical constants, and the chemical reactions of perchloryl fluoride were investigated by A. ENGELBRECHT and H. ATZWANGER at the Chemical Institute of the University of Innsbruck, Austria. The preparation with elemental fluorine, the determination of the critical data, and additional experiments, were carried out by A. ENGELBRECHT at the Pennsylvania Salt Manufacturing Co. Research and Development Department, Whitemarsh Research Laboratories, Wyndmoor, Pa. The authors are indebted to Professor E. HAYEK, Head of the Department of Chemistry University of Innsbruck, Austria, for his interest and encouragement during the course of this investigation; and to Miss RUTH KOSSATZ (infra-red absorption spectrum determination), of the Pennsylvania Salt Manufacturing Co. Research and Development Department, Whitemarsh Research Laboratories, Wyndmoor, Pennsylvania.

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J. Inorg. Nucl. Chem., 1956, Vol. 2, pp. 358 to 367. Pergamon Press Ltd., London

PLUTONIUM HEXAFLUORIDE

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(*Received* 1 *December* 1955)

Abstract—The preparation of plutonium hexafluoride by the fluorination of plutonium trifluoride, tetrafluoride, or dioxide is described, and the effect of temperature, rate of flow of fluorine, duration of reaction, and nature of the starting material is discussed in some detail. The formula PuF_6 has been confirmed by chemical analysis.

Some properties of plutonium hexafluoride are described, these include the vapour pressure, melting-point, decomposition under α-particle irradiation, and reactions with water and sulphuric acid.

SEVERAL observations by workers at A.E.R.E., Harwell, suggested that plutonium forms a volatile compound, possibly a fluoride. For example, milligram quantities of plutonium trifluoride, plutonium(IV) oxalate, or plutonium dioxide were completely volatile in a stream of hydrogen fluoride and oxygen[1] at temperature above 700°C. By analogy with the reaction

$$UF_4 + O_2 = UO_2F_2 + UF_6$$

it was assumed that plutonium hexafluoride had been produced, and milligram quantities of a volatile plutonium compound were, in fact, obtained by passing oxygen over plutonium tetrafluoride at 850°C.[2] Consequently, the action of fluorine on plutonium compounds was investigated, with successful production of plutonium hexafluoride. The method of preparation and some physical and chemical properties of the hexafluoride are presented below.

The preparation of plutonium hexafluoride. The principal reactions by which plutonium hexafluoride is formed are now known to be:

	Refs.
(1) $2PuO_2 + 12HF + \frac{1}{2}O_2 \rightarrow 2PuF_6 + 6H_2O$	(1)
(2) $PuF_4 + O_2 \rightarrow PuF_6 + (?PuO_2F_2)$	(2)
(3) $PuF_4 + F_2 \rightarrow PuF_6$	(3, 4, 5)
(4) $2PuF_3 + 3F_2 \rightarrow 2PuF_6$	(4)
(5) $PuO_2 + 3F_2 \rightarrow PuF_6 + O_2$	(this report)

Reaction (3) has been studied in detail in the present work, and observations have been made on reactions (4) and (5).

DESCRIPTION OF APPARATUS AND EXPERIMENTAL PROCEDURE

In outline, the experimental procedure for the preparation of PuF_6 was to pass pure fluorine through a nickel furnace containing PuF_4 heated to 600°C. Volatile reaction products were condensed

[1] J. K. DAWSON and A. E. TRUSWELL, *A.E.R.E. C/R* 662 (1951).
[2] C. J. MANDLEBERG *et al. A.E.R.E., C/M* 157 (1952).
[3] C. J. MANDLEBERG *et al. A.E.R.E., C/R* 1172 (1953).
[4] A. E. FLORIN, I. R. TANNENBAUM, and J. F. LEMONS, *J. Inorg. Nucl. Chem.* **2**, 368 (1956).
[5] B. WEINSTOCK and J. G. MALM, *J. Inorg. Nucl. Chem.* **2**, 380 (1956).

in a nickel trap cooled in liquid oxygen. The apparatus was then evacuated and any volatile products distilled into a suitable container. In all, six furnaces were constructed, differing only slightly in dimensions.

Considerable difficulty was experienced in constructing an apparatus which was resistant to fluorine and other corrosive vapours at 600–700°C, and which could also be evacuated to 10^{-3}–10^{-4} mm Hg. Details of the constructional methods adopted have already been reported by two of the present authors,[16] and only the apparatus itself will be described here. A schematic diagram is shown in Fig. 1. The flow-rate from the fluorine cylinder was controlled by a specially constructed reducing valve, and the fluorine passed through flexible bronze-bellows tubing to point *A*. Point *B* was connected to a supply of argon, which was purified by passage over silica gel and

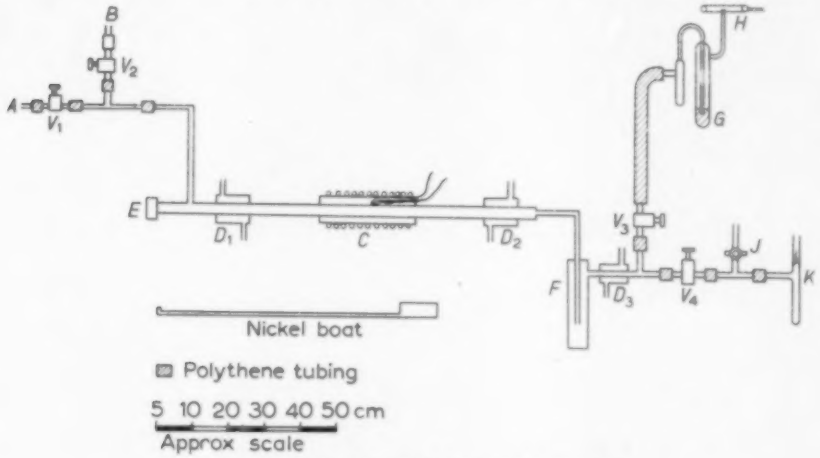

FIG. 1.—Schematic diagram of fluorination apparatus.

magnesium perchlorate, and then over calcium metal heated to 300°C. The argon, now free from oxygen and all but the last traces of water vapour, was condensed in a bead trap surrounded by liquid nitrogen, and finally evaporated slowly at liquid-oxygen temperature; the middle fraction was considered to be pure enough to use to purge the apparatus.

The nickel furnace *C* was heated by resistance wire wound around a spirally grooved silica tube. A Pt/Pt-Rh thermocouple was placed in contact with the outside of the nickel wall of the furnace. Each end of the furnace was cooled by water jackets D_1 and D_2. By means of a wire spot-welded to it, a nickel boat was pushed into the furnace at *E*, which was then closed with a brass screwed cap and a P.T.F.E. gasket.

The nickel condensing trap was at *F*; the water jacket D_3 protected the adjacent polythene connector from severe cooling.

The fluorine left the apparatus through a sulphuric-acid bubbler *G*. This was made of glass, and had previously been calibrated so that the absolute gas flow-rate could be deduced from the bubbling rate.

At *J* was attached a conventional pumping system consisting of rotary and diffusion pumps, and glass liquid-oxygen traps.

The apparatus was fluorinated at 600°C, using fluorine and then uranium hexafluoride. After purging with pure argon, the apparatus was evacuated for some days to remove all volatile fluorination products. Dry argon was then readmitted and the reaction boat containing PuF_4 placed in the furnace.

The fluorine was purified by passing it through a brass tank immersed in liquid oxygen, and it was then admitted to the apparatus at V_1. The nickel trap *F* was surrounded by liquid oxygen and the furnace heated to a temperature in the range 320° to 720°C and maintained to ±10°C of the chosen temperature for the duration of the run. The flow-rate of the fluorine was adjusted to about 1–2 mmoles per minute, and the run allowed to proceed for several hours. On cooling, the apparatus was

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purged with dry argon and then evacuated to a pressure of $<5\mu$ for several minutes. After the system had been isolated from the pumps, liquid oxygen was placed around the receiving vessel *K*, and the trap *F* was gently heated. The volatile material was allowed to distil for 1–2 hours, after which the receiving vessel was pumped out while at liquid-oxygen temperature, and then isolated from the system. Two types of receiving vessel were used, either a standard glass or silica breaker-seal tube, which could be isolated by sealing off under vacuum, or a nickel reservoir, $\frac{1}{2}$ in. in diameter and 9 in. deep, closed with one of the vacuum valves described elsewhere.[6]

CONDITIONS FOR THE REACTION OF PLUTONIUM TETRAFLUORIDE WITH FLUORINE

Early in the present work it was recognized that the reaction was not a simple one; the rate of the reaction seemed to depend not only on the reaction temperature, but also on the fluorine flow-rate, the initial mass of plutonium tetrafluoride, the previous history of the plutonium tetrafluoride, and the period during which the reaction had proceeded. Under certain conditions, the tetrafluoride not used up in the reaction was considerably altered. The effect of each of these factors has been studied in some detail, and is discussed below. The experimental results obtained in a number of runs producing plutonium hexafluoride by this reaction are given in Tables 1, 2, and 3.

It should be pointed out that the conditions were not ideal for studying a gas solid reaction. The corrosive nature of the gaseous reactant and of the principal product, the high temperature involved, and, above all, the precautions necessary to handle plutonium compounds in greater than gram quantities (in particular, relatively large quantities of a volatile plutonium compound), have hindered the work.

(a) *The effect of temperature on the reaction.* The reaction is a slow one, very much slower than the analogous preparation of uranium hexafluoride at the same temperature. Thus, at 400°C in our present apparatus, UF_4 was fluorinated to UF_6 at a rate of about 4 g per hour, whereas, under the same conditions, PuF_6 was formed from PuF_4 at a rate of about 200 mg per hour. The rate of the reaction is increased by increasing the temperature in the range 320° to 620°C, as is shown in Table 1.

TABLE 1.—EFFECT OF TEMPERATURE ON REACTION RATE
(Duration of reaction — 4 h)

Run	Initial wt. of PuF_4 (g)	Temp. (°C)	Mean rate of reaction (mg PuF_4 per hour)
74	3·00	320	0
73	3·02	370	125
72	3·04	420	230
71	3·15	470	348
70	3·18	520	490
69	2·92	570	600
61	3·03	620	635
62	3·00	620	533
63	2·96	620	612
64	3·06	620	588
65	2·96	620	545

(b) *The influence of fluorine flow-rate.* If the fluorine flow-rate falls below 0·2 mmoles per minute, the rate of the reaction is considerably reduced. However, at high flow-rates (20 mmoles per minute), the rate of the reaction is not significantly increased above its value at a flow-rate of one mmole per minute. Even the lowest of these flow-rates is greater than the uptake of fluorine calculated from the rate of formation of PuF_6 (0·05 mmole min^{-1} at 620°C).

[6] C. J. MANDLEBERG and H. K. RAE, *A.E.R.E. C/M* 172 (1953).

It seems likely that the rate-controlling factor is the diffusion of the fluorine into, and of the plutonium hexafluoride out of, the grains of tetrafluoride, and that the rapid removal of the product from the reaction zone ensures a high partial pressure of fluorine at the grain surfaces and hence a high rate of reaction. A fluorine flow-rate of one mmole per minute was used in nearly all the present work.

TABLE 2.—EFFECT OF INITIAL CHARGE OF PuF_4 ON THE REACTION RATE

Run	Furnace	Temperature (°C)	Time (h)	Initial wt. of PuF_4 (g)	Mean rate of reaction (mg PuF_4/hour)
37	5	630	11	4·97	305
38	5	630	11	7·16	380
34	5	670	5·7	1·29	104
32	5	670	5·7	1·90	160
57	6	720	4	3·02	550
66	6	720	4	5·00	705

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TABLE 3.—EFFECT OF THE METHOD OF PREPARATION OF PuF_4 ON THE RATE OF FLUORINATION

Run	Furnace	PuF_4		Temp. (°C)	Time (h)	Residue wt. (g)	Mean reaction rate (mg/hour)
		wt	Temp. of prep. (°C)				
17	3	1·05	350	640	4·2	0·10	226
24	3	0·94	350	630	2·5	0·26	272
31	4	2·41	550	625	10·8	0·75	154
32	4	1·90	550	675	5·8	1·00	155
34	4	1·29	550	675	5·8	0·70	102
35	4	1·45	350	620	4·9	0·10	275
40	5	1·86	550	635	4·2	0·62	295
47	5	1·88	550	630	5·3	0·87	190
49	5	2·34	350	630	5·0	0·65	338
39	5	1·17	(from PuF_3) 190	640	3·0	0·44	243

(c) *Effect of the weight of the PuF_4 charge.* The rate of reaction (see Table 2) is greater the greater the charge, but the relationship is not a simple one.

(d) *The effect of the previous history of the plutonium tetrafluoride.* Plutonium tetrafluoride was prepared from plutonium(IV) nitrate solution by first precipitating the oxalate with a solution of oxalic acid at 80–90°C, removing the supernatant liquid, and igniting the oxalate slurry to the oxide in a stream of argon and oxygen. This oxide was then converted to the tetrafluoride by the action of hydrogen fluoride and oxygen, under the following different temperatures of ignition and hydrofluorination respectively:—(i) 550° and 550°, (ii) 350° and 550°, (iii) 350° and 350°C. The material prepared by any of these methods was pale pink in colour. By far the largest number of runs were performed with material prepared by method (ii).

A series of observations of the reaction rate of plutonium tetrafluoride made under these conditions is set out in Table 3, where it is seen that, the rate of the reaction of the tetrafluoride with fluorine is diminished appreciably by an increase in the temperature used for ignition and for hydrofluorination, the most reactive material being that prepared by ignition and hydrofluorination at 350°C.

A single experiment (Run 39) was carried out using tetrafluoride prepared by the reaction

$$2PuF_3 + F_2 \xrightarrow{190°C} 2PuF_4$$

(e) *The rate of reaction in relation to time of contact.* The mean rate of the reaction decreased as the overall reaction time was increased. The results of several series of experiments which show this are plotted in Fig. 2, the reaction conditions being constant for each family of points. The data for one such family (III in Fig. 2) are shown in Table 4.

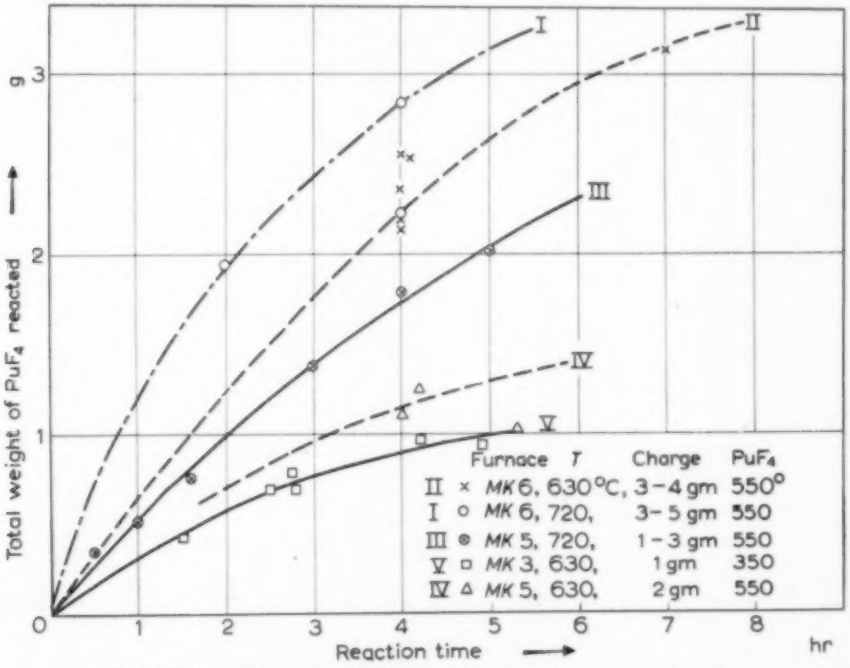
Total weight of PuF4 reacted g
Reaction time hr
I
II
III
IV
V
Furnace T Charge PuF4
II × MK 6, 630°C, 3–4 gm 550°
I ○ MK 6, 720, 3–5 gm 550
III ● MK 5, 720, 1–3 gm 550
V □ MK 3, 630, 1 gm 350
IV △ MK 5, 630, 2 gm 550

FIG. 2.—The dependence of total PuF_4 reaction upon duration of fluorination.
Abscissa:—Reaction time (h).
Ordinate:—Total weight of PuF_4 reacted (g).

TABLE 4.—THE RATE OF REACTION IN RELATION TO TIME OF CONTACT
A typical set of results.

Run	Time interval (h)	Wt. of PuF_4 remaining unreacted (g)	Average rate over time interval (mg/h)
53	0–0·5	2·650	700
54	0·5–1·0	2·485	330
55	1·0–3·0	1·635	425
52	3·0–4·0	1·215	420
56	4·0–5·0	1·005	210

This series of reactions was carried out at 720°C, using a charge of 3·0 g of plutonium tetrafluoride prepared by ignition and hydrofluorination at 550°C.

Reaction of plutonium dioxide with fluorine. Plutonium dioxide was prepared by igniting freshly precipitated plutonium(IV) oxalate. This material was then fluorinated in a furnace similar to that used for the fluorination of PuF_4. The results of the fluorination at low temperatures were not reproducible, and seemed to indicate that the previous history of the PuO_2 was important, but at temperatures above 400°C the reaction proceeded in two well-defined stages, PuF_4 being first produced and this being subsequently fluorinated to PuF_6 in the usual way. At 600°C, the overall rate of the conversion was about 400 mg/h and was thus comparable with the fluorination of the tetrafluoride under the same conditions.

PROPERTIES OF PLUTONIUM HEXAFLUORIDE

Analysis of the volatile fluoride. Although there is little doubt as to the formula of the volatile fluoride of plutonium, it was felt desirable to confirm its composition by chemical analysis. This was carried out by hydrolysis and subsequent determination of the Pu : F ratio. Because of the vigorous nature of the hydrolysis at room temperature (see below), the hydrolysis was carried out by condensing PuF_6, which had been pumped at −70°C for some hours, on to ice on a glass cold finger at −180°C, sealing off the cold trap, and allowing the system to warm up to room temperature. The hydrolysis took place smoothly under these conditions to give an orange-pink solution. The glass trap was cracked open and washed out with dilute sulphuric acid. The solution was examined spectrophotometrically, and the plutonium found to be substantially in the hexavalent state.

The solution was analysed for fluorine by distillation of hydrofluoric acid from the acid solution and subsequent titration, and for plutonium by the counting of aliquots. The ratio Pu : F was found to be $1 : 6{\cdot}26 \pm 0{\cdot}38$; thus confirming the formula PuF_6.

Physical Properties

Appearance and melting-point. Plutonium hexafluoride, when condensed in a dry Pyrex or silica tube at −180°C and sealed *in vacuo*, is a white crystalline solid, similar in appearance to uranium hexafluoride. On warming to room temperature, the solid turns to a pale brown which deepens as the temperature is increased, the solid melting at 54 ± 1°C to a limpid dark-brown liquid. The vapour at the melting-point is pale brown and at 70°C a deep brown.

Vapour pressure. This was determined at various temperatures by means of a bellows manometer which was used as a null-point instrument, the backing pressure required to return the bellows to the fiduciary mark being observed on a mercury-in-glass manometer by means of a cathetometer. Before any readings were made, the reservoir of hexafluoride was maintained at −70°C and evacuated continuously for sixty hours to remove traces of hydrofluoric acid. When this precaution was not taken, appreciably higher values of the vapour pressure were obtained. The series of measurements extended over three weeks, and it was found that, although the apparatus was free from leaks, a pressure of a gas which was incondensable at −80°C, slowly developed. This was attributed to the decomposition of PuF_6 to a lower fluoride and fluorine under its own α bombardment (see below). Consequently, before making a series of measurements, the reservoir was cooled to −70°C and pumped to remove the incondensable gas. The vapour pressure was measured over the temperature

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range −29·5 to + 21°C (vapour-pressure range 0·8 to 97·4 mm Hg) and the points are closely represented by the equation (see Fig. 3)

$$\log_{10} P_{\text{mmHg}} = 11{\cdot}45 - 2{\cdot}778 \cdot 10^3/T\,^{\circ}\text{K}.$$

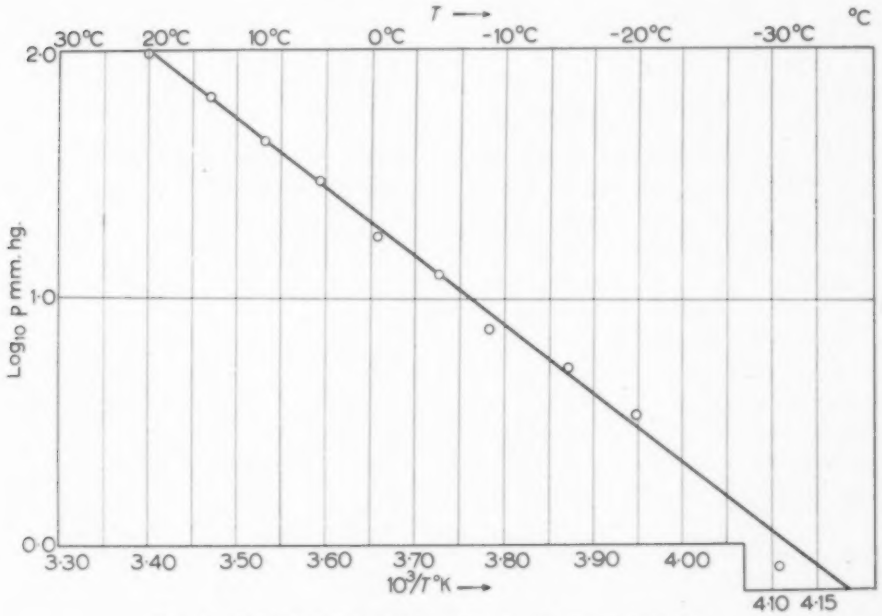

FIG. 3.—Vapour pressure of PuF_6, $\log_{10} P_{\text{mmHg}}$ versus $10^3/T\,^{\circ}$K.
Abscissa:—(bottom) $10^3/T\,^{\circ}$K, (top) $T\,^{\circ}$C.
Ordinate:—$\text{Log}_{10} P_{\text{mmHg}}$

Decomposition of plutonium hexafluoride. On standing for several days in a sealed container, plutonium hexafluoride produces a free-flowing pink solid (from which residual hexafluoride can be removed by sublimation), and a corresponding rise in pressure occurs. This is attributed to disruption of the molecule under the bombardment of the plutonium α particles. Immediately on coming in contact with moist air in the glove-box, the pink powder darkened slightly. Samples of this phase were examined on a quartz helix balance and thermogravimetric curves in air obtained; a distinct plateau was observed at 150° to 230°C for all the samples. On cooling from 200°C, an increase in weight of 1% occurred. At higher temperatures there was further loss of weight, and at 500°C in air the samples were completely converted to the dioxide.

The original decomposition product gives no X-ray diffraction pattern, presumably because of the small size of the particles deposited during the decomposition of the hexafluoride; its chemical analysis is given in column A below. The diffraction pattern of the compound formed by heating in air to 200°C was found to be identical with that of a compound reported by DAWSON and D'EYE,[7] which was shown to be a hydrate of plutonium tetrafluoride containing between 0·5 and 1·5 molecules of water

[7] J. K. DAWSON, R. W. M. D'EYE, and A. E. TRUSWELL *J. Chem. Soc.* 3922 (1954)

(cf. the analysis below at *B*). Both compounds were analysed for plutonium by ignition to the dioxide and for fluorine by pyrohydrolysis.

	A Original product	*B* After heating to 200°C
Plutonium	70·0%	72·4%
Fluorine	22·2%	23·4%
Water (?) by difference	7·8%	4·2%
F : Pu atomic ratio	3·99	4·03
Formula	$PuF_4 \cdot 1{\cdot}5H_2O$	$PuF_4 \cdot 0{\cdot}8H_2O$

Thus the product of the decomposition of plutonium hexafluoride is the tetrafluoride, and the darkening on bringing the product into contact with moist air is attributed to the rapid formation of the hydrate, $PuF_4 \cdot 1{\cdot}5H_2O$.

Rate of decomposition. The rate of decomposition was determined by two methods: by weighing the amount of solid decomposition product produced, and (b) by observing the pressure rise during the decomposition.

(a) *Solid formation.* The amount of solid produced by decomposition of the hexafluoride was determined by weighing as $PuF_4 \cdot 1{\cdot}5\ H_2O$. Vessels of nickel and glass were used, the latter being kept at −70°C during the experiment. Sufficient hexafluoride (ca. 1 g) was introduced into the vessels to ensure that some solid hexafluoride remained at the end of the experiment. The amount of tetrafluoride produced after different times, varying from six to thirty-six days, was determined, giving an average value for the decomposition rate of about 10 mg of hexafluoride decomposed per day (i.e. about 1% per day) for the particular vessel used.

(b) *Pressure rise.* The rise in pressure during the decomposition was observed in the same apparatus as that used to determine the vapour pressure of plutonium hexafluoride. The reservoir of hexafluoride was kept at room temperature during the experiment, but when readings of pressure were made the reservoir was cooled in ice. The experiment covered a period of thirty-four days. During the first eleven days, while solid PuF_6 was estimated, by mass balance, to be still present, the pressure rise was linear with time; but after the eleventh day the rate of rise in pressure decreased, following an exponential law. Under the conditions of the experiment, the total rate of decomposition in the vapour was 2% per day. However, the estimated range of plutonium α particles in the vapour (approx. 5 cm) was so much greater than the size of the reservoir (cylinder, 1-cm dia., 20 cm long) that the greater part of the energy of the α particles would be lost to the walls.

REACTIONS OF PLUTONIUM HEXAFLUORIDE

Reaction with water. Plutonium hexafluoride can be stored at room temperature in carefully dried Pyrex glass for long periods, and with undried glass there is normally no reaction at −180°C. On warming an undried tube containing the hexafluoride from −180°C, a brown flaky stain spreads rapidly over the whole of the inside of the tube, accompanied by considerable etching. The reaction does not appear to go to completion as readily as that of uranium hexafluoride, for after some period of hydrolysis a considerable quantity of plutonium hexafluoride can be distilled from the tube. The product of this hydrolysis is plutonyl fluoride, PuO_2F_2, as demonstrated by X-ray diffraction (isomorphous with UO_2F_2) and by weight change on conversion to dioxide.

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On hydrolysis with water or moist air at room temperature, a violent reaction takes place, accompanied by flashes of light. The resulting solution contains a variable amount of precipitate which has been shown by X-ray analysis to contain PuF_4 hydrate and PuO_2, demonstrating further the high temperatures occurring during the hydrolysis. No evidence was found for the presence of valency states other than the hexavalent in the solution resulting from the hydrolysis.

Reaction with sulphuric acid. During the fluorination of the tetrafluoride the effluent fluorine was passed through a bubbler of 98% sulphuric acid, which served to prevent the diffusion of water vapour into the apparatus. After a time this acid became pink in colour and eventually threw down a flocculent pink precipitate which on standing separated out as a pink crystalline solid. If the acid and precipitate were left standing in moist air, the precipitate redissolved to give a bright-red solution.

The crystalline precipitate was filtered under suction on a porous disk, but could not be washed, as it dissolved in sulphuric acid or water. On standing, however, it gave a friable brick-red powder. The X-ray diffraction pattern of this powder is very complex, and agrees closely with that of $U(SO_4)_2 \cdot 2H_2O$. The powder was analysed by dissolving in dilute nitric acid, the plutonium being determined by α-counting and the sulphate by precipitation as barium sulphate, giving the following values:— Pu 41·8%, SO_4 37·0%; water (?) by difference 11·2%. This corresponds to $Pu(SO_4)_2 \cdot 0{\cdot}2\ H_2SO_4 \cdot 3{\cdot}5\ H_2O$ which represents the formula of the above sample of the precipitate. The solution in 98% sulphuric acid was examined in the spectrophotometer,[8] and the absorption spectrum agrees closely with that for Pu(IV) in 16 M sulphuric acid.[9]

Thus the analytical, X-ray diffraction, and spectrophotometric evidence make it highly probable that the pink precipitate produced when plutonium hexafluoride is passed into sulphuric acid is plutonium (IV) sulphate, although the mechanism of the reaction

$$PuF_6 \xrightarrow[H_2SO_4]{F_2} Pu(SO_4)_2$$

is obscure.

NOTE ON AN INTERMEDIATE OF FLUORIDE OF PLUTONIUM

It was observed that under certain conditions the residue remaining in the furnace after a fluorination was darker in colour than the original tetrafluoride. Below 500°C the residue was apparently unchanged in colour, but above this temperature the residue became progressively darker, the proportion which had been changed and the depth of colour of the new material increasing with increasing reaction temperature and time of contact. At 600°C some of the residue from a few grams of starting material was still pink even after a few hours contact, and it was observed in every case that this apparently unaltered pink material overlay the brick-red residue. These residues were analysed, the fluorine being determined by the pyrohydrolytic method, where the error is probably not more than ±0·2 units per cent fluorine. It is possible that the gross error was somewhat greater than this, because at these elevated temperatures the attack of the fluorine upon the nickel of which both the furnace and the boat were constructed, was not negligible, and it was difficult to obtain samples totally free from

[8] The authors are indebted to Messrs. G. R. HALL and A. WALTER for these measurements

[9] J. C. HINDMAN *National Nuclear Energy Series* Division IV Volume 14A Chapter 9 (McGraw-Hill 1954)

flakes (canary yellow) of nickel fluoride, but, in those sent for analysis, the nickel fluoride was not visible to the naked eye, and was certainly less than 1% by weight. Plutonium tetrafluoride contains 24·1% fluorine, and NiF_2 39·3% fluorine, so that nickel-fluoride contamination will lead to high analytical figures for the fluorine in the tetrafluoride, but 1% by weight of nickel fluoride would only make the apparent fluorine percentage in PuF_4 too high by 0·15 unit per cent.

The analytical results for various samples of this residue are set out in Table 5.

TABLE 5.—FLUORINE ANALYSES OF THE RESIDUE REMAINING AFTER FLUORINATION

Run	PuF_4 preparation	Reaction temperature (°C)	% F
33	From oxide	675	25·8
39	From PuF_3	640	26·3
42	From oxide	720	25·9
43	From oxide	770	25·7

(cf. Calculated values for PuF_4 24·1%, Pu_4F_{17} 25·3%, Pu_2F_9 26·3% fluorine)

A number of X-ray diffraction photographs of this material, prepared in different runs, were taken, and compared with those of PuF_4 prepared as described above. PuF_4 has a monoclinic cell and the diffraction pattern is rather complicated. Only visual comparison of the films has so far been possible; it was seen that the patterns from the various residues are always very well defined and much more distinct than those of PuF_4. This may be due to recrystallization which has taken place at the high temperature. Moreover, the majority of lines present are common to the photographs both of PuF_4 and of the residue, but there are a number of minor differences which make the PuF_4 residue pattern rather similar to the "distorted UF_4" lattice, which was reported by AGRON *et al.*[10] and subsequently identified as U_4F_{17} on the basis of chemical analysis, and which has been observed by two of the present authors.[11]

In view of the chemical and X-ray evidence, we conclude that the brick-red residue is an intermediate fluoride of plutonium, probably Pu_4F_{17}.

[10] P. A. AGRON *et al.*, *U.S. Atomic Energy Commission Report* MDDC 1588 (1948)
[11] C. J. MANDLEBERG and D. DAVIES, *A.E.R.E. C/R* 863 (1952)

J. Inorg. Nucl. Chem., 1956, Vol. 2. pp. 368 to 379. Pergamon Press Ltd., London

PREPARATION AND PROPERTIES OF PLUTONIUM HEXAFLUORIDE AND IDENTIFICATION OF PLUTONIUM(VI) OXYFLUORIDE*

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(*Received* 22 *July* 1955)

Abstract—The compound plutonium hexafluoride has been identified and characterized. A method of preparation by the fluorination of plutonium tetrafluoride is outlined. The vapour pressure, which corresponds closely to that of uranium hexafluoride, has been measured between 0 and 63°C. The vapour pressure is represented by the equations:

$$\text{Log}_{10} P_{\text{liquid}}\,(\text{mm}) = 7{\cdot}6923 - \frac{1614{\cdot}3}{T}$$

$$\text{Log}_{10} P_{\text{solid}}\,(\text{mm}) = 10{\cdot}841 - \frac{2634{\cdot}3}{T}$$

The boiling-point is 62·3°C. The heat of sublimation is calculated to be 12·1 kcal/mole. The melting-point is 50·7°C. The heat of vaporization is 7·4 kcal/mole. The heat of fusion is 4·7 kcal/mole, and the corresponding entropy of fusion is 14·5 cal/mole °C.

A study of the equilibrium, $PuF_4 + F_2 \rightleftharpoons PuF_6$, has resulted in values of 11·5 kcal/mole and 7·8 e.u. for ΔH and ΔS in the temperature range from 167 to 308°C. Respective values of 6·77 and −0·3 were obtained in the range from 308 to 600°.

The rates of thermal decomposition and radio-decomposition have been considered.

A solid compound produced when plutonium hexafluoride was exposed to moist air was identified as plutonium(VI) oxyfluoride, PuO_2F_2.

INTRODUCTION

THE possible existence of plutonium hexafluoride was postulated by many investigators soon after the isolation of plutonium and the discovery that its properties were remarkably similar to the properties of uranium. Studies at that time with tracer quantities of plutonium produced contradictory results, but it was observed that if fluorine gas was passed over a plutonium compound at about 500°C, the plutonium distilled from the hot zone and deposited in the cooler zones. Similar experiments with hydrogen fluoride substituted for fluorine produced no volatile plutonium fluoride and indicated that only the higher-valence plutonium fluoride was volatile. BROWN and HILL,[1] using microgram quantities of plutonium in a series of distillation experiments with uranium hexafluoride, concluded that the higher fluoride of plutonium is unstable in the absence of fluorine and decomposes to plutonium tetrafluoride over a period of hours at room temperature. They also concluded that the vapour pressure of the plutonium compound was about the same as that of uranium hexafluoride. DAVIDSON, KATZ, and ORLEMANN[2] conducted experiments in which plutonium was volatilized from a hot nickel filament in an atmosphere of

*This work was done under the auspices of the U.S. Atomic Energy Commission.

(1) H. S. BROWN and O. F. HILL *University of Chicago Metallurgical Laboratory Report CN*-363, November 31, 1942.

(2) N. R. DAVIDSON, J. J. KATZ, and E. F. ORLEMANN *University of Chicago Metallurgical Laboratory Report CK*-987, October 11, 1943.

fluorine directly onto a cold platinum surface. The plutonium deposited at temperatures as high as room temperature and did not redistill at temperatures as high as 200°C, indicating that the compound was not volatile at this temperature or had been converted to a nonvolatile compound.

At a later date, the problem was reinvestigated, using milligram quantities of plutonium. In general, the results of this work were as inconclusive and difficult to explain as the early experiments. However, FISHER, VASLOW, and TEVEBAUGH[3] interpreted some of their experiments as evidence that the higher fluoride has a positive heat of formation and is stable only at high temperatures in an atmosphere of fluorine. Their tentative conclusion was that the higher fluoride might be condensed rapidly to a point where the rate of decomposition would be low, but on heating to revolatilize, the compound would be expected to decompose even in a stream of fluorine unless the temperature were raised to 350 to 550°C. FLORIN[4] prepared a volatile compound of plutonium which was presumed to be plutonium hexafluoride, although it decomposed before its identity could be established. In this experiment the volatile material was condensed on a glass surface at low temperature, and after ageing for a few minutes the compound became less volatile and changed from solid to liquid. This behaviour was interpreted as evidence of reaction of the fluoride with the glass surface.

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To predict the properties of plutonium hexafluoride, BREWER, BROMLEY, GILLES, and LOFGREN[5] made use of existing thermodynamic data plus reasonable estimates of other data, based principally on the relation between the behaviour of corresponding plutonium and uranium compounds. They concluded that it would have somewhat greater stability than it has now been shown to have. Also, it was predicted that plutonium hexafluoride would be gaseous and have a boiling point slightly above room temperature.

More recent work by FLORIN and others is summarized in a series of reports,[6] but has not been published previously.

Subsequent to the completion of most of the work reported here, investigations have been reported in England by MANDLEBERG, RAE, DAVIS, and FRANCIS[7] and by HURST, MANDLEBERG, RAE, DAVIS, and FRANCIS.[8] Additional studies in this country are reported by MALM and WEINSTOCK[9] and HAWKINS, MATTRAW, and SABOL.[10]

PREPARATION OF PLUTONIUM HEXAFLUORIDE

A suitable procedure for the preparation of plutonium hexafluoride involves the endothermic reaction

$$PuF_4 + F_2 \rightleftarrows PuF_6(g)$$

[3] R. W. FISHER, F. VASLOW, and A. D. Tevebaugh *Iowa State College, Report CN*-1783, August 10, 1944.
[4] A. E. FLORIN *University of Chicago Metallurgical Laboratory Report CN*-2159, October 1, 1944.
[5] L. BREWER, L. BROMLEY, P. W. GILLES, and N. L. LOFGREN *University of California Radiation Laboratory Report CN*-3300, October 10, 1945, and *Report CN*-3378, December 1, 1945.
[6] A. E. FLORIN *Los Alamos Scientific Laboratory Reports LAMS*-1118, October 16, 1950; *LA*-1168, November 9, 1950; *LAMS*-1587, September, 1952; and I. R. TANNENBAUM and A. E. FLORIN, *LA*-1580, May 15, 1953.
[7] C. J. MANDLEBERG, H. K. RAE, D. DAVIS, and K. E. FRANCIS *Atomic Energy Research Establishment Report A.E.R.E. C/R* 1172, April 1953.
[8] R. HURST, C. J. MANDLEBERG, H. K. RAE, D. DAVIES, and K. E. FRANCIS *Atomic Energy Research Establishment Report A.E.R.E.-C/R*-1312, January 1953.
[9] J. G. MALM and B. WEINSTOCK *Argonne National Laboratory Report ANL*-5366, September, 1954.
[10] N. J. HAWKINS, H. C. MATTRAW, and W. W. SABOL *Knolls Atomic Power Laboratory Report KAPL*-1007, May 24, 1954.

at a temperature of about 700°C. The rate increases with faster fluorine flow over the solid, and the yield increases when the plutonium hexafluoride is cooled very rapidly. The conventional tube-furnace technique for carrying out a reaction of this type in which the gas is passed over a boat containing the solid has been used successfully for the preparation of plutonium hexafluoride. However, this method proved to be slow and inefficient, especially when it was desired to convert small quantities rather completely. The apparatus finally developed is an elaboration of the Sainte-Claire Deville hot-cold tube technique, which provides for rapid freezing of the product in close proximity to the high-temperature reaction zone, and is especially effective for carrying out endothermic reactions that produce a volatile product which can be condensed as a metastable phase at a temperature which is too high to condense any volatile reactants.

The reactor for the preparation of plutonium hexafluoride is illustrated in Fig. 1.

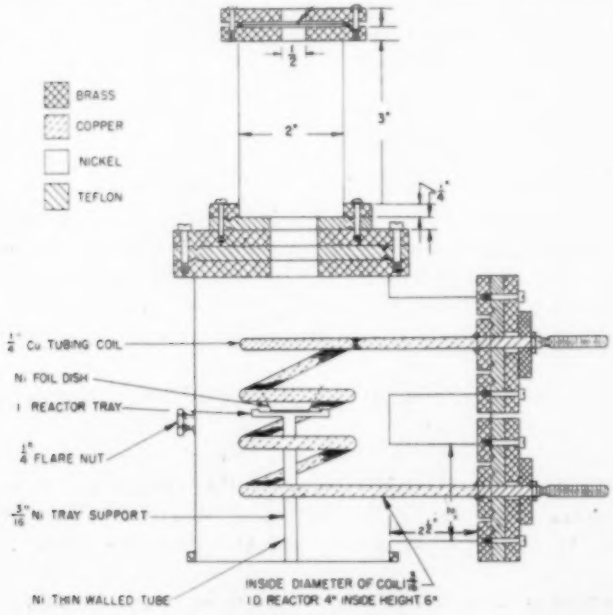

FIG. 1.—Fluorination reactor.

The reactor consists of a brass can containing a cylindrical dish, which holds the plutonium tetrafluoride, supported axially within the work coil of an induction heater. The coil for the induction heat is cooled with liquid nitrogen. The dish is located in close proximity (1/32-in. clearance) to the induction coil in order to provide a cold surface for freezing out the plutonium hexafluoride before it has an opportunity to decompose in the zone of intermediate temperature. The high-temperature gradient and large temperature difference between the reactor dish and the refrigerated coil presumably set up strong convection currents which promote the rapid transfer of plutonium hexafluoride from the boat to the collection coil. The boat is operated at about 700°C, and the fluorine pressure is about 30 cm, the vapour pressure of liquid fluorine at the temperature of the refrigerated coils.

In a typical preparation, as soon as the dish containing the plutonium tetrafluoride

reaches red heat, a white condensate begins to form on the cooling coils. After the end of the operation period, the induction heater is turned off and excess fluorine is pumped from the reactor. The cooling coils are allowed to warm to room temperature, and the plutonium hexafluoride is condensed into a nickel storage vessel.

Plutonium hexafluoride can be produced at the rate of about 1 g/hr in this apparatus with as much as 90% yield, based on plutonium tetrafluoride consumed.

Flow of gases is controlled through a double system of manifolds (Fig. 2). The

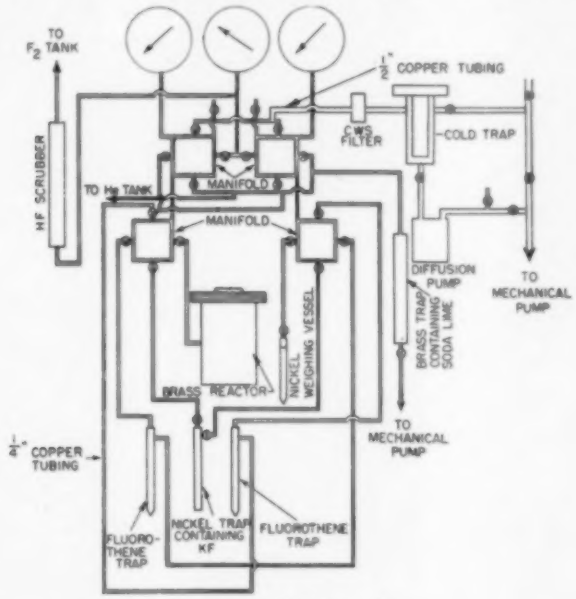

FIG. 2.—Fluorination system.

upper manifolds provide connection to vacuum pumps and fluorine and helium supply lines. Helium is used as an inert flushing gas to keep moist air out of the reactor when it is open for loading with plutonium tetrafluoride. The lower manifolds are used to distribute the services brought in through the upper manifolds. Connected to the lower manifolds are the preparation reactor, various traps, etc., for studying properties of plutonium hexafluoride.

All parts of the apparatus exposed to fluorine and plutonium hexafluoride are constructed of materials which are relatively inert to corrosion by fluorine. These materials include nickel, monel, copper, brass, silver solder, and Teflon and Fluorothene plastics. In addition to extensive use of flared fittings, closures and connections are either welded, silver-soldered, or Teflon- or Fluorothene-gasketed. Before use, all equipment was thoroughly cleaned and conditioned with fluorine, according to customary procedures.

PHYSICAL AND THERMODYNAMIC PROPERTIES OF PLUTONIUM HEXAFLUORIDE

X-ray Pattern

The identification of plutonium hexafluoride is based on a single X-ray diffraction pattern. Only a weak pattern was obtained, but it indicated clearly that the plutonium

compound was isomorphous with both uranium hexafluoride and neptunium hexafluoride. The data indicate that plutonium hexafluoride has a slightly smaller unit cell size than uranium hexafluoride, as would be expected from an actinide contraction effect. A comparison of the X-ray diffraction patterns for plutonium, uranium,[11] and neptunium[12] hexafluorides is given in Table 1. The uranium hexafluoride structure was solved by HOARD and STROUPE.[13] They found that uranium hexafluoride is orthorhombic with the D_{2h}^{16}-Pn*ma* space group. The lattice constants are: $a_0 = 9{\cdot}95$ Å, $b_0 = 9{\cdot}02$ Å, $c_0 = 5{\cdot}26$ Å.

TABLE 1.—A COMPARISON OF X-RAY DIFFRACTION PATTERNS* FOR PLUTONIUM, URANIUM, AND NEPTUNIUM HEXAFLUORIDES

PuF_6		UF_6		NpF_6	
$\sin^2\theta$	Intensity	$\sin^2\theta$	Intensity	$\sin^2\theta$	Intensity
		0·0223	*w*	0·0224	*vvw*
				0·0279	*vw*
0·0294	*mw*	0·0293	*w*	0·0290	*s*
0·0317	*mw*	0·0315	*w*	0·0319	*s*
0·0354	*mw*	0·0352	*w*	0·0353	*s*
				0·0463	*w+*
0·0577	*w*	0·0574	*w*	0·0575	*s−*
0·0760	*w*	0·0757	*w*	0·0764	*m+*
0·0842	*vw*	0·0834	*w*	0·0838	*w*
0·0912	*w*	0·0908	*w*	0·0904	*w+*
0·0944	*vw*			0·0956	*w−*
0·1005	*vw*			0·1008	*w*
0·1062	*w*			0·1062	*w+*
				0·1124	*vw*
0·1178	*vw*			0·1184	*w*
0·1265	*w*	0·1265	*w*	0·1261	*w*
		0·1343	*w*		
0·1428	*w*	0·1420	*w*	0·1431	*w+*
0·2104	*w*				
0·2398	*w*	0·2384	*w*		
0·2632	*vw*				
0·3035	*w*				
0·3394	*vw*	0·3385	*vw*		
0·3589	*vw*	0·3560	*vw*		

* All patterns were obtained with copper *K*α radiation.

Physical Appearance

As it condenses on refrigerated coils in the preparative apparatus, solid plutonium hexafluoride is white. After distillation from the apparatus, it is light brown in colour and is finely crystalline. On standing at room temperature, the crystals increase in size and the colour deepens to a red-brown.

The liquid phase has also been observed to be brown in colour.

[11] F. H. ELLINGER, private communication, April 1949.
[12] W. H. ZACHARIASEN, private communication, August 1949.
[13] J. L. HOARD and J. D. STROUPE, *Cornell University Report A*-1242, March 1, 1944.

Vapour Pressure of Plutonium Hexafluoride in the Region from 0 *to* 63°C

The apparatus for measuring the vapour pressure consists of a thermostated copper U-tube, which contains the plutonium hexafluoride, connected to a Booth-Cromer,[14] null-diaphragm type, self-balancing, pressure gauge. The copper U-tube is mounted in a Dewar flask through which thermostated water is circulated. Immediately above this flask and in contact with the bath liquid is mounted a second thermostated bath consisting of an insulated metal can of sufficient size to hold the pressure gauge and necessary auxiliary equipment, including a stirrer, heater, and thermoregulator. The valves which close the copper U-tube are located in this second thermostat, which is maintained at a temperature approximately five degrees above the temperature of the lower bath. This arrangement is necessary to keep solid or liquid plutonium hexafluoride out of the gauge, where it would interfere with the diaphragm action. Silicone oil was chosen for the bath liquid because of its favourable electrical insulating properties. The temperature of the vapour pressure U-tube was maintained at the specified temperature to within about 0·02°. However, since the upper bath is not cooled below room temperature except as a result of heat loss to the lower bath, the conduction of heat into the lower vapour-pressure vessel at low temperature makes the temperature of the plutonium hexafluoride somewhat uncertain at the lower temperatures.

The balancing pressure for the diaphragm gauge is measured with a mercury manometer. The manometer was read with a precision of 0·01 mm. All the necessary conventional corrections were applied to convert these readings to true pressure readings.

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Pressure data obtained for the temperature range 0 to 63°C for plutonium hexafluoride are shown as a plot of log $P_{\text{mm Hg}}$ (corrected to 0° and standard gravity) vs. $1/T$°K in Fig. 3. The different shapes of points on the graph represent different samples of plutonium hexafluoride. For comparison, the same data for uranium hexafluoride as selected by KIRSHENBAUM[15] is also shown in Fig. 3. It is seen that approximately linear relationships are obtained. This indicates that the purity of the sample is good. The slight curvature of the data toward pressures in excess of those predicted by a straight-line function at temperatures below room temperature probably results from experimental error. As already described, in this temperature range a thermal gradient as great as 25° existed between sample tube and gauge; therefore, the temperature of the sample is subject to some question.

From Fig. 3 it is seen that plutonium hexafluoride is less volatile than uranium hexafluoride, but the difference is small.

The vapour-pressure curves for the liquid and solid plutonium hexafluoride in the temperature range between 15 and 60°C may be expressed by the following equations:

$$\log_{10} P_{\text{liquid}}\,(\text{mm}) = 7{\cdot}6923 - \frac{1614{\cdot}3}{T}$$

$$\log_{10} P_{\text{solid}}\,(\text{mm}) = 10{\cdot}841 - \frac{2634{\cdot}3}{T}$$

The average deviation of points from the line in Fig. 3 is 1·1% if data at temperatures below 15°C are excluded; however, this value does not necessarily reflect possible errors due to the following: small amounts of impurities which might either raise or lower the pressure, faulty gauge action (due to deposition of solid decomposition products of plutonium hexafluoride in the diaphragm chamber of the gauge), improper correction of observed pressure for partial pressure of fluorine gas, or failure to attain

[14] S. CROMER *Columbia University SAM Laboratory Report A*-1286, April 18, 1944.
[15] I. KIRSHENBAUM *Columbia University SAM Laboratory Report A*-753, July 1, 1943. See Also B. WEINSTOCK and R. H. CRIST *J. Chem. Phys.* **16**, 436 (1948); G. D. OLIVER, H. T. MILTON, and J. W. GRISSARD *J. Amer. Chem. Soc.* **75**, 2827 (1953).

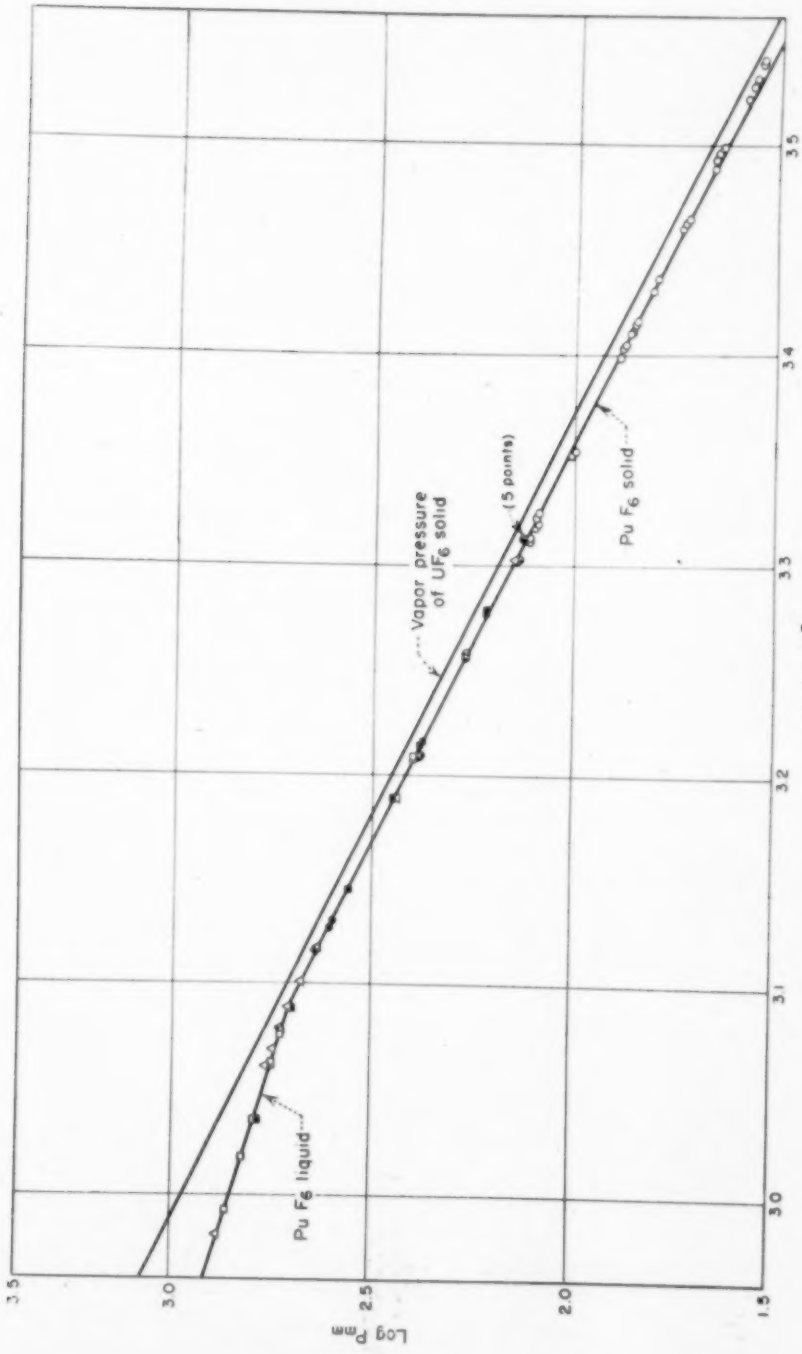

FIG. 3.—Vapour pressure of plutonium hexafluoride.

equilibrium between solid or liquid and gas phases of plutonium hexafluoride. This last source of error may have been greater than would usually be encountered, because of the continuous evolution of fluorine gas from plutonium hexafluoride, and the fact that the sample and gauge are connected by a tubing of less than 1/16-in. internal diameter. No limit of error has been assigned to any of the results, although it is felt the results as given are probably correct to better than 2 or 3%.

Heat of Sublimation

From the slope of the line drawn for plutonium hexafluoride in Fig. 3, the heat of sublimation is calculated to be 12·1 kcal/mole. The value obtained from the uranium hexafluoride line is 11·89 kcal.

Triple Point

The intersection of solid and liquid lines shown in Fig. 3 gives a triple point for plutonium hexafluoride at 50·7°C and 511 mm Hg. The triple point for uranium hexafluoride occurs at 64·05°C and 1135 mm Hg.

Melting has also been observed visually at the triple point, but the liquid phase appeared to attack the fluorothene container, and melting occurred over several degrees temperature range.

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Heat of Vaporization

The value calculated from the slope of the liquid-vapour line in Fig. 3 is 7·4 kcal/mole for the heat of vaporization of plutonium hexafluoride. From the data given by KIRSHENBAUM,[15] the heat of vaporization of uranium hexafluoride can be extrapolated to the temperature range used in calculating the value for plutonium hexafluoride. The value for the heat of vaporization of uranium hexafluoride obtained in this way is 7·15 kcal.

Heat and Entropy of Fusion

The difference between heat of sublimation and heat of vaporization gives 4·7 kcal/mole as the heat of fusion. The entropy of fusion is then 14·5 cal/mole °C.

For uranium hexafluoride, KIRSHENBAUM[15] gives 4·588 kcal for heat of fusion and 13·61 cal/mole °C for entropy of fusion.

Boiling-point

The boiling-point of plutonium hexafluoride obtained from Fig. 2 is 62·3°C. Uranium hexafluoride sublimes with a pressure of 1 atm at 56·5°C.

Trouton's Constant

From values of the boiling-point and heat of vaporization of plutonium hexafluoride, Trouton's Constant is calculated to be 22·0.

Absorption Spectrum of the Liquid

A laboratory bench-type Bausch and Lomb spectrometer was used to obtain a very crude visual absorption spectrum of liquid plutonium hexafluoride in a fluorothene tube held just above the triple-point temperature. The spectrum, given in millimicrons, contained a prominent band at 560 to 565, weaker bands at 542 to 546 and 578 to 590, and almost complete absorption below 525.

The Plutonium Tetrafluoride-fluorine-plutonium Hexafluoride Equilibrium

The equilibrium $PuF_4 + F_2 \rightleftharpoons PuF_6$ was studied at several temperatures in both the forward and reverse directions by analysing the gas phase of the equilibrium

mixture for both plutonium hexafluoride and fluorine. From these equilibrium data, ΔH, ΔF, and ΔS for the reaction have been calculated.

The reaction chamber for establishing the equilibrium is shown in Fig. 4. It consists of a welded nickel can (2 in. O.D. × 2 in. long) with a special high-temperature nickel valve at one end. The reaction chamber is connected through the valve by nickel and copper tubing to a manifold to which plutonium hexafluoride or fluorine can be supplied and from which samples can be withdrawn for

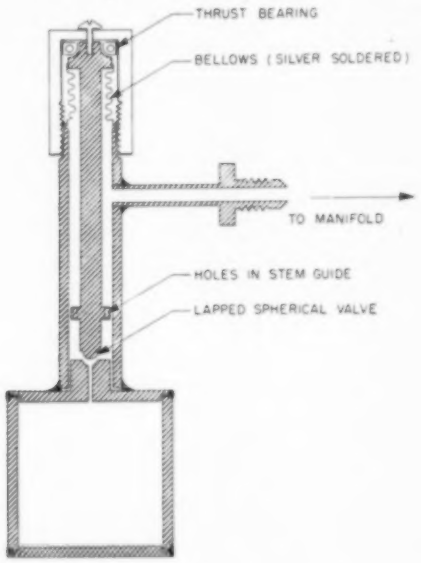

FIG. 4.—Equilibrium chamber and high-temperature valve.

analysis. To study the decomposition of plutonium hexafluoride, a sample of plutonium hexafluoride is distilled into the reaction chamber and the valve closed. The reaction chamber is heated to the temperature at which an experimental point is desired and kept at that temperature for a sufficient time (from several minutes to a few hours, depending on the temperature) to permit the reacting materials to approach equilibrium. At the end of that time the nickel valve is opened and the volatile contents of the reactor are pumped out through the manifold into the analysis apparatus. It is assumed that these gases represent the equilibrium concentrations of plutonium hexafluoride and fluorine. In the analysis apparatus, plutonium hexafluoride is frozen out in a liquid-nitrogen cold trap and later washed out of the cold trap with nitric acid and determined by alpha counting. The fluorine passes through the cold trap into a tube filled with sodium bromide at 150°C, where fluorine is exchanged for bromine. The bromine is frozen out in a liquid-nitrogen cold trap and later allowed to react with a solution of potassium iodide to produce a solution of iodine in potassium iodide. This final solution is titrated with 0·1 N thiosulphate to determine iodine. The amount of fluorine emerging from the reaction chamber is equal to the amount of iodine found in the titration.

After several determinations of the equilibrium, using plutonium hexafluoride as the starting material, enough plutonium tetrafluoride is deposited in the reaction chamber so that it is only necessary to add fluorine to the system to permit approach to equilibrium in the forward direction. After addition of fluorine, the procedure for these runs is the same as described above.

The equilibrium constant K for the reaction $PuF_4 + F_2 \rightleftharpoons PuF_6$, at each temperature T can be written $K = \dfrac{[PuF_6]}{[F_2]}$. From a plot of log K vs. $1/T$ (see Fig. 5) two

straight-line relations appear to fit the data. The equations for the straight lines are $\log_{10} K = -2{\cdot}51 \times 10^3/T + 1{\cdot}71$ and $\log_{10} K = -1{\cdot}48 \times 10^3/T - 0{\cdot}06$ for the temperature ranges 167 to 308°C, and 303 to 600°C respectively. Values for the heat of reaction, ΔH, have been calculated from the slopes of these curves. The free energy of reaction, ΔF, was obtained by applying the relation $\Delta F = -RT \ln K$, where R is the gas constant. The entropy of reaction, ΔS, was obtained from the relation $\Delta F = \Delta H - T\Delta S$. The equilibrium data and calculated quantities are summarized in Table 2.

TABLE 2.—THERMODYNAMIC VALUES FOR THE REACTION $PuF_4 + F_2 \rightleftharpoons PuF_6$

Temperature (°C)	$K = \frac{[PuF_6]}{[F_2]}$	ΔF (kcal/mole	ΔH (kcal/mole)	ΔS (cal/mole °C)
167	0·0001	+8·05		
200	0·00025	+7·8		
300	0·0021	+7·0		
400	0·0055	+6·97		
500	0·011	+6·99		
600	0·017	+7·03		
167 to 308			+11·5	+7·8
308 to 600			+6·77	−0·3

The ΔH values show an increase from +6·7 to +11·5 kcal/mole with decreasing temperature. On the basis of the limited data shown in Fig. 5, the change appears to take place at one temperature rather than gradually over a range of temperatures. This would suggest the possibility that the change results from a phase change in the reacting material.

Since plutonium fluorides intermediate in composition between plutonium tetrafluoride and plutonium hexafluoride, and of uncertain stability and volatility, may exist in the equilibrium mixture, some doubt may be justly raised concerning the accuracy and applicability of the measured equilibrium values. It is thought, however, that such intermediate fluorides, even if shown to exist, would have little or no effect on the measured equilibrium values. Thus far, the only reproducible data have been obtained at elevated temperature with plutonium hexafluoride present only in the gas phase.

It is of interest to note that the equilibrium constant increases with temperature, i.e. plutonium hexafluoride is less dissociated as the temperature is increased.

Radio-decomposition of Plutonium Hexafluoride

Pressure has been observed to increase slowly with time in a closed system containing solid plutonium hexafluoride in equilibrium with its vapour. The decomposition rate has been measured by observing the rate of pressure rise due to fluorine evolution when a known amount of plutonium hexafluoride decomposes in a known volume. The decomposition rate has been found to be independent of temperature within experimental error over the range 0 to 50°C; although with increasing temperature there is an initial rapid rise in pressure which slowly decreases to a constant rate after a few

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hours. This behaviour is presumed to result from the degassing of the solid compound mass. On the assumption that the decomposition products are fluorine and plutonium tetrafluoride, plutonium hexafluoride decomposes initially at the rate of $1{\cdot}3 \pm 1\%$ per day. Less accurate information on decomposition over intervals as long as nine months indicates a rate at least as low as 0·9% per day and probably as low as

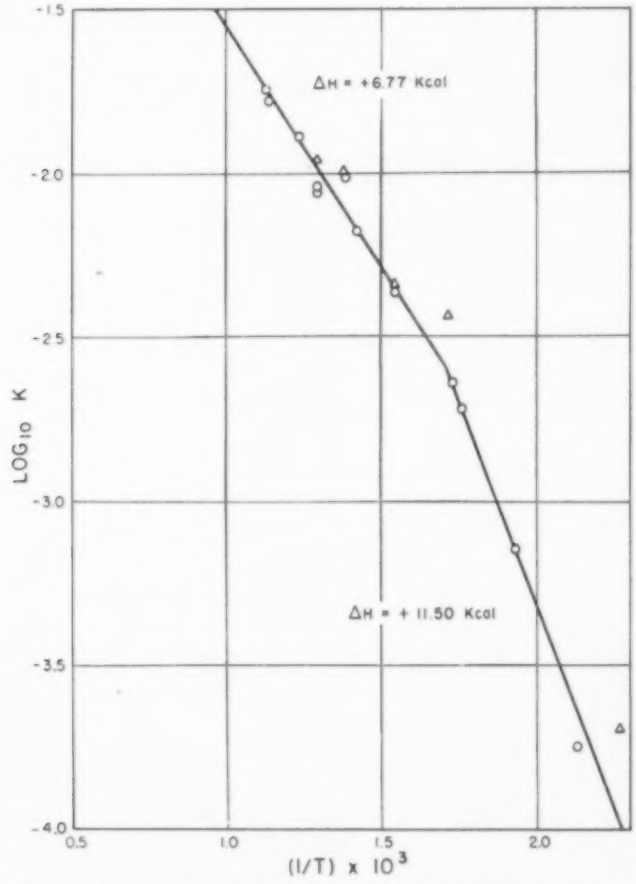

FIG. 5.—Equilibrium data for the reaction $PuF_4 + F_2 \rightleftharpoons PuF_6$. Symbols ○ and △ indicate forward and reverse approaches to equilibrium.

0·6% per day. These data imply that the decomposition rate decreases with increasing age of material.

If it is assumed that the decomposition results from alpha radiation, the yield corresponds to about 31 e.v. per molecule of plutonium hexafluoride decomposed. This calculation is based on the assumption that alpha particles are emitted at the rate of $1{\cdot}4 \times 10^5$ per minute per microgram of plutonium, with an average energy of 5·1 MeV, and that the energy is 100% absorbed. The last assumption should be sensibly correct for the solid material. Decomposition in the pure vapour state has not been investigated.

Thermal Decomposition of Plutonium Hexafluoride

The constant rate of decomposition in the temperature range from 0 to 50°C suggests that the contribution of a thermal rate in this temperature-range is within the limit of error established for alpha-induced decomposition. Probably it is much smaller.

The products of high-temperature thermal decomposition have not been firmly established. However, finely divided plutonium tetrafluoride has been observed to grow large crystals, approximately 1 mm in length, under elevated temperature conditions in which plutonium hexafluoride vapour is known to exist. This behaviour suggests the existence of an equilibrium involving plutonium tetrafluoride and hexafluoride.

An experiment, in which plutonium hexafluoride in a nickel can was decomposed at 540°C, produced more than 1 gram-atom of fluorine per mole of plutonium hexafluoride and established that the product of decomposition has less fluorine than plutonium pentafluoride. It is probable that the decomposition product is plutonium tetrafluoride, since data by LANDAU and ROSEN[16] for the corrosion of nickel can account for the discrepancy in the fluorine balance.

Identification of Plutonium(VI) Oxyfluoride

When plutonium hexafluoride was exposed to moist air in a fluorothene tube, a solid product was formed. An X-ray diffraction pattern showed isomorphism with the compound UO_2F_2; consequently, the compound is presumed to have the analogous formula PuO_2F_2.

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Acknowledgement—The authors wish to acknowledge the assistance of F. H. ELLINGER in making and interpreting the X-ray diffraction patterns.

[16] R. LANDAU and H. ROSEN *Kellex Corporation Report A*-2921.

J. Inorg. Nucl. Chem., 1956, Vol. 2, pp. 380 to 394. Pergamon Press Ltd., London

THE PROPERTIES OF PLUTONIUM HEXAFLUORIDE*

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(*Received* 6 *January* 1956)

Abstract—PuF_6 is formed rapidly at 750°C by the reaction between PuF_4 and F_2, and high yields are obtained if the PuF_6 is quickly condensed. AmF_6 is not produced under similar conditions. Techniques for the handling, purification, and storage of PuF_6 are described. The molecular structure and crystal structure of PuF_6 are the same as those of UF_6. The melting-point of PuF_6 is 50·75°C. Radiation decomposition of PuF_6 into PuF_4 and F_2 occur at the rate of 1·5% per day for the solid phase. The rate of radiation decomposition is much smaller in the vapour phase, and the system may reach a steady state. Solid PuF_6 is slightly paramagnetic. The absorption spectrum of PuF_6 vapour shows six groups of bands between 5000 and 25,000 Å, arising from electronic transitions in the molecule. PuF_6 is a strong fluorinating agent, and its reactions with BrF_3, UF_4, and PuF_3 are described. Thermal decomposition of PuF_6 is not observed at room temperature, but is found to be very rapid at 280°C. The equilibrium constant for the dissociation of PuF_6 into F_2 and PuF_4 is $1{\cdot}86 \times 10^8$ at 220°C; at 25°C, $\Delta F^\circ = -7{\cdot}6$ kcal mole^{-1}, $\Delta H^\circ = -8{\cdot}3$ kcal mole^{-1}, and $\Delta S^\circ = -2{\cdot}3$ cal mole^{-1} deg^{-1} for this dissociation.

PLUTONIUM hexafluoride is the volatile plutonium analogue of uranium hexafluoride. Its existence was suggested in the nineteen-forties by many experimenters because of the volatility exhibited by plutonium compounds in fluorinating gas streams at elevated temperatures. These early workers, however, did not successfully isolate PuF_6, and ascribed their failure to its instability to dissociation. The first successful isolation and identification of this compound was reported in October 1950 by A. E. FLORIN.[1] Second-hand verbal accounts of the work of British investigators with this compound[2] were also communicated to us prior to the start of our work.

Method of Preparation

The reactor that we have used for the preparation of PuF_6 is shown schematically in Fig. 1, and is similar to one used by FLORIN, TANNENBAUM, and LEMONS.[1] Plutonium tetrafluoride contained in a nickel dish *A* is heated in a fluorine atmosphere (300 mm Hg pressure) by the work coil of an induction heater *F* that is located within the reactor. This coil, which is made of copper tubing, is cooled by the circulation of liquid nitrogen and therefore serves not only as the heating mechanism but also as the condenser for the PuF_6 that is produced. The clearance between the coil and the nickel dish is 1·6 mm, and this proximity of hot and cold areas provides a very efficient convection mechanism for the removal of the volatile product from the hot crucible to the condenser. It will be shown later that PuF_6 is less stable at lower temperatures; therefore, to obtain a high yield, it is necessary to chill the product rapidly to temperatures where the rate of dissociation is slow.

* Based on work performed under the auspices of the U.S. Atomic Energy Commission.
[1] A. E. FLORIN, I. R. TANNENBAUM, and J. F. LEMONS *J. Inorg. Nucl. Chem.* **2**, 368 (1956).
[2] C. J. MANDLEBERG, H. K. RAE, R. HURST, G. LONG, D. DAVIES, and K. E. FRANCIS *ibid.* **2**, 358 (1956).

Good vacuum conditions are necessary to avoid losses of PuF_6 due to hydrolytic decomposition. The weakest points of the reactor assembly from the point of view of vacuum tightness are the electrically insulated closures *H* required for the copper-tubing induction-heater leads. These must not leak despite thermal cycling from liquid-nitrogen to room temperatures. This problem was solved by a design that restricted the plastic flow of the Teflon and by a procedure whereby the final tightening

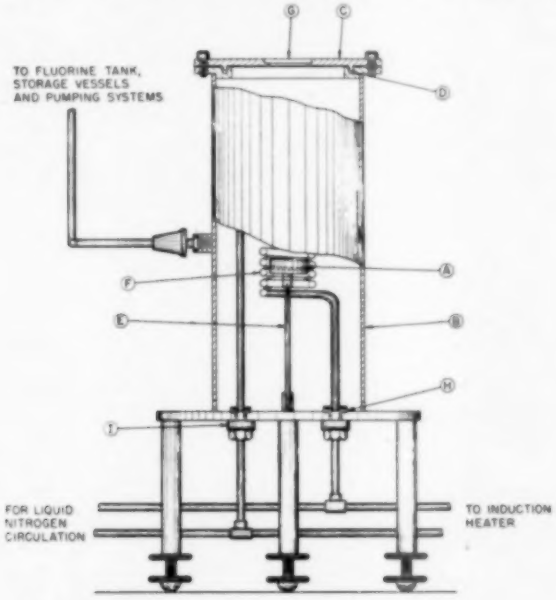

FIG. 1.—Reactor for plutonium hexafluoride

A Nickel dish filled with PuF_4.
B Brass reactor can.
C Removable cover for loading reactor.
D Tongue and groove; Teflon gasket for closure.
E Nickel supporting rod for nickel dish.
F Coil of 3/16-in. o.d. copper tubing.
G Fluorothene window.
H Teflon seal and insulator.
I Micalex insulator.

of the Teflon was made at liquid-nitrogen temperature. A helium leak detector was used to locate leaks. In addition, the criterion was used that the steady-state pressure in the reactor system be less than 10^{-5} mm Hg prior to the introduction of fluorine.

In our preparations, 1-g quantities of PuF_4 have been used. A Flourothene window *G* provided in the top of the reactor permitted measurement of the temperature of the nickel dish with an optical pyrometer and also permitted visual observation of the reaction. No significant change in the appearance of the PuF_4 was noted until a temperature of about 750°C was reached, at which time a dense cloud formed above the heated dish. The appearance of this cloud was taken as an indication of the rapid formation of PuF_6. When the "smoke" cleared after five to ten minutes, the crucible appeared to be substantially free of PuF_4 and the reaction was considered complete. After permitting the nickel dish to cool, most of the fluorine was disposed of by pumping it through a soda-lime bed. The reactor was finally pumped down to a

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pressure of about 10^{-5} mm Hg, with a high vacuum line, before warming the coils and transferring the PuF_6 to the storage system (Fig. 2) by distillation. The PuF_6 was separated from hydrogen fluoride, as described later, before measurement. The yield of purified PuF_6 was assayed by P-V-T measurement, and generally was at least 90% of the amount calculated for complete conversion of the charge. This method for the evaluation of the yield of PuF_6 was used in preference to a calculation based on the amount of unconverted PuF_4 remaining in the nickel dish. The latter method would give a result which is too optimistic if losses of PuF_6 occur prior to its collection.

Attempt to Prepare Americium Hexafluoride

An unsuccessful attempt was made to prepare AmF_6 under the same conditions in which PuF_6 is obtained in high yield. In this experiment, 2 mg of americium oxide was added to 860 mg of PuF_4 and the mixture treated with fluorine in the manner that was just described. The fluorine gas that was used contained sufficient hydrogen fluoride to insure the rapid conversion of the oxide to the corresponding fluoride under the conditions of the experiment. Although the volatile product obtained in this experiment corresponded to 90% of the starting material, Am was not detected in it. The molar ratio of Am to Pu in this gas was determined to be less than 0·004% by alpha-pulse analysis[3] compared to the starting composition of 0·23% Am; the sensitivity of the alpha-pulse analysis was limited in this case by the similarity of the alpha energies of Am^{241} and Pu^{238}. A sample of the solid residue remaining in the crucible was found to have the AmF_3 structure[4] by the X-ray powder technique. This experiment indicates that either AmF_6 requires more vigorous treatment than PuF_6 for its preparation or cannot be prepared at all. It is of some interest to note that this method of preparation for PuF_6 provides a good separation of Pu from Am.

Comparison of the Preparations of the Actinide Hexafluorides

PuF_6 can be prepared rapidly at a temperature of about 750°C and a fluorine pressure of 300 mm Hg; under these same conditions AmF_6 is not produced. NpF_6 can be produced rapidly in a somewhat different-type reactor at 500°C[5] and UF_6 at 300°C.[6] This qualitative comparison shows that the actinide hexafluorides are produced with increasing difficulty as one proceeds through the series uranium, neptunium, plutonium, and americium, with the possibility that AmF_6 cannot be prepared. This behaviour is analogous to the increasingly negative value found for the IV-VI oxidation potentials of these elements in aqueous solutions, which G. T. SEABORG has suggested is partial evidence for an actinide series.[7]

Method of Handling, Purification, and Storage

Because of the peculiar difficulties presented by the study of a highly radioactive and reactive gas such as PuF_6, we describe here our methods of handling, purification, and storage. A schematic diagram of the storage and purification system is shown in

[3] A. GHIORSO, A. H. JAFFEY, H. P. ROBINSON, and B. WEISSBOURD, Paper 16.8, *The Transuranium Elements*, *N.N.E.S.*, IV-14*B*, McGraw-Hill Book Co., New York (1949), SEABORG, KATZ, and MANNING, ed.
[4] W. H. ZACHARIASEN, Chap. 18. *The Actinide Elements*, *N.N.E.S.* IV-14*A*, McGraw-Hill Book Co., New York (1954), SEABORG and KATZ, ed.
[5] J. G. MALM and B. WEINSTOCK, unpublished work.
[6] Chap. 13, *The Chemistry of Uranium*, *N.N.E.S.* VIII-5, Part I, McGraw-Hill Book Co., New York (1951), KATZ and RABINOWITCH, ed.
[7] G .T. SEABORG, Chap. 17, *The Actinide Elements*, *N.N.E.S.* IV-14*A*, McGraw-Hill Book Co., New York (1954), SEABORG and KATZ, ed.

Fig. 2. The fittings *C*, *D*, *I* and valves *B* are of the high-pressure design (30,000 p.s.i.) for use with $\frac{3}{8}$-in. o.d. heavy-wall seamless tubing. These are usually available commercially in stainless steel, but for the present application, the metal parts that are exposed to PuF_6 have been fabricated with Monel and nickel and the packing rings in the valves replaced with Teflon.[8] The Monel or nickel U-tubes G_1 and G_2,

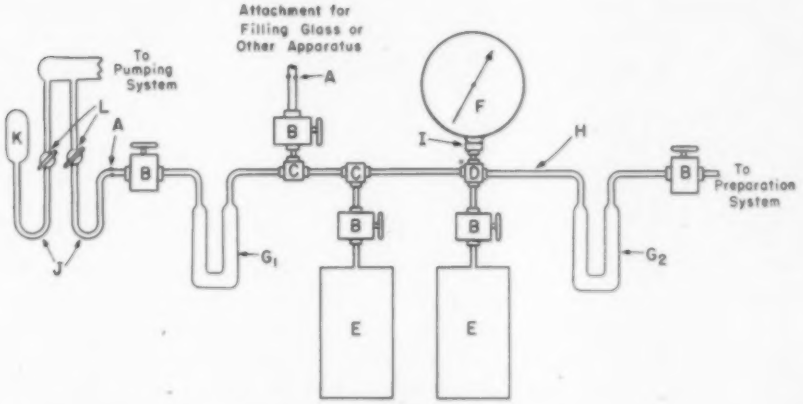

FIG. 2.—Purification and storage system.

A Kovar to Pyrex seal.
B 30,000 p.s.i. Valve, Monel body, Teflon packing.
C 30,000 p.s.i. Monel Tee.
D 30,000 p.s i. Monel Cross.
E 1500 cc capacity welded nickel storage cylinder.
F Welded Monel Bourdon gauge 0–1500 mm.
G Welded nickel U-tubes.
H Seamless Monel tubing $\frac{3}{8}$ in. o.d. × $\frac{1}{4}$ in. i.d.
I Monel gauge connector, pipe thread connection to gauge soft soldered on outer threads.
J Pyrex glass U-tubes.
K Glass Phillips-type ionization gauge.
L Stopcocks.

storage containers *E*, and Bourdon gauge *F* are of all-welded construction. The system was given a reduction with hydrogen and fluorination with fluorine prior to use with PuF_6. A connection to a three-stage, glass oil-diffusion pump is provided through a Kovar-glass seal *A*. Some darkening of the Octoil-S in this pump has occurred due to small exposures to fluorine, but no loss in pumping speed or ultimate vacuum has as yet become apparent. By comparison, a mercury diffusion pump given similar treatment would probably have had to be replaced, due to constrictions formed by the deposition of mercury fluoride. A glass U-tube *J* kept at −78°C protects the storage system from stopcock grease-vapour. A glass Phillips-type ionization gauge is used to measure the pressure; its protecting U-tube is cooled with solid CO_2 (−78°C) rather than liquid nitrogen, so that the presence of hydrogen fluoride will be detected.

The use of high-pressure equipment for the metal purification and storage system is based on our experience that good vacuum conditions can be readily obtained and maintained in such systems. The high-vacuum technique was required since many of our experiments were to be carried out in Pyrex and quartz apparatus, where the

[8] Supplied by Autoclave Engineers, Inc., Erie, Pa., U.S.A.

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complete separation of hydrogen fluoride from the PuF_6 was essential in order to avoid the continual hydrolytic decomposition of the PuF_6. (A chain reaction is set up in which HF reacts with the glass to produce water, which in turn hydrolyses PuF_6 to re-form HF.)

The method of purification from HF consisted of two steps. The PuF_6 to be purified is first completely vaporized in one of the storage containers E and then slowly condensed there with a solid CO_2-trichloroethylene bath. The condensed solid is then pumped on until the steady-state pressure in the system is about 10^{-5} mm Hg. During this operation the bulk of the HF is removed, because the vapour pressure of HF is of the order of several mm Hg while that of PuF_6 is of the order of a micron. Continued pumping on the condensed PuF_6 will not remove the remainder of the HF that is trapped in the solid. This separation is effected by cooling U-tube G_1 with solid CO_2 and allowing the storage container to warm slowly while the pumping is continued. Under these conditions little occlusion of HF by PuF_6 occurs, owing to the very small pressure maintained in the system. The removal of HF during this operation is qualitatively indicated by an increased reading of the ion gauge. If the PuF_6 is then distilled into U-tube G_2 and the last step repeated by distilling the PuF_6 from U-tube G_2 to G_1 while pumping, only a slight rise in ion-gauge reading is observed, indicating the absence of HF. Quartz and Pyrex equipment, after thorough outgassing, have been filled with PuF_6 purified in this way without the use of getters, and show no signs of hydrolytic decomposition after long standing (twenty months).

The plutonium hexafluoride is generally handled with equipment mounted on a hooded vacuum frame grid. Sliding doors are provided to permit ready access, and a ventilating air flow of 1500 cfm is provided. In transporting PuF_6 sealed in fragile containers for study in other areas, completely sealed secondary containers are provided, and optical measurements, for example, are made through a double set of windows. These precautions are rather minimal in nature and have not been tested as yet by an accident. Little difficulty has been met with maintaining a low activity level in the laboratory, although a wide variety of experiments has been carried out.

Identification and Chemical Composition

The similarity in volatility and method of preparation between the plutonium compound and uranium hexafluoride suggest that the two have a similar chemical composition. This has been confirmed by a direct chemical analysis. A 262-mg sample of purified "PuF_6" was sealed off in a Pyrex tube and its weight determined by difference between the empty and filled tube. The PuF_6 (condensed in the bottom of this tube with solid CO_2) was then hydrolysed with an ammoniacal solution admitted through a break-seal. This hydrolysis occurred with greater vigour than had been our experience with UF_6, and may have resulted in some loss of sample. The fluoride content was determined by distilling fluosilicic acid from the solution and titrating the distillate with $Th(NO_3)_4$.[9] The plutonium content was determined by alpha counting; the Pu^{238}, Pu^{240}, and Pu^{241} content being determined by mass spectrometer and pulse analysis and the specific activity of Pu^{239} corrected for their presence. The results were: F, 30·9 $\pm$ 0·6% (theoretical, 32·3%); Pu, 66·5 $\pm$ 2·0% (theoretical, 67·7%);

[9] G. W. BUSCH, R. C. CARTER, and F. E. MCKENNA, Chap. 5 *Analytical Chemistry of the Manhattan Project, N.N.E.S.* VIII-1, McGraw-Hill Book Co. (1950), C. J. RODDEN, ed.

atomic ratio F/Pu = 5·83. The atom ratio of F to Pu of 5·83 is in satisfactory agreement with the formula PuF_6.

The purity of the PuF_6 used in these studies has been established by infra-red studies, where absorption bands due to other known volatile fluorides have not been observed. The similarity of the infra-red spectrum of this substance with UF_6 is further evidence for the formula PuF_6.[10]

The identification of this material as PuF_6 has been also established by an X-ray powder photograph taken in a thin-walled glass capillary. The pattern obtained showed the sample to be isostructural with solid UF_6.[11]

Physical Properties

Solid plutonium hexafluoride, as observed in glass, is yellowish brown in colour; when freshly condensed with liquid nitrogen it also appears as bright red crystals. The vapour is brown in colour and resembles nitrogen tetroxide. The melting-point has been determined to be 50·75 ± 0·1°C in a thin-walled Pyrex X-ray capillary. For this determination the capillary was strapped to the bulb of a thermometer, immersed in a clear mineral-oil bath, and was observed with a microscope. The PuF_6 was first distilled to the top of the capillary by raising the capillary partly out of the bath and cooling the exposed section. The melting-point was then obtained by completely immersing the capillary and slowly raising the temperature of the bath until the solid melted and the liquid droplet ran down the tube. Under these conditions the solid (10-μ crystallites) appeared amber in colour and the liquid pale yellow.

Approximate vapour-pressure measurements show that PuF_6 is slightly less volatile than UF_6.[12] The vapour density determined at 25°C and 20–100-mm pressure indicates that PuF_6 is probably monomeric in the vapour phase.

Radiation Decomposition

The alpha activity of Pu^{239}, $1{\cdot}36 \times 10^{11}$ dis/min/g, not only presents a serious health hazard in the study of the properties of PuF_6, but also causes a continuous destruction of the PuF_6 by radiation decomposition into fluorine and a lower plutonium fluoride. The decomposition product obtained from the radiation decomposition of solid PuF_6 is green in colour under vacuum and turns white upon exposure to air. Both the green and white solids have been identified as tetravalent plutonium fluorides by X-ray analysis. Solution of the decomposition product in dilute acidic $Al(NO_3)_3$ and examination of the solution spectrophotometrically confirmed the presence of the tetravalent oxidation state. The trivalent and pentavalent states were not detected, but some hexavalent plutonium was found. The presence of the hexavalent state can be accounted for on the basis of an incomplete removal of PuF_6 from the solid decomposition product, although the possibility of an intermediate oxidation state between 4 and 6 which disproportionates into the 4 and 6 states upon solution cannot be discounted.

The rate of radiation decomposition in solid PuF_6 has been determined to be 1·5% per day in two experiments, one of which lasted 24 hours and the other 6·9 days. The method was to seal off a measured amount of PuF_6 in a Pyrex tube, and after the

[10] J. G. Malm, B. Weinstock, and H. H. Claassen *J. Chem. Phys.* **23**, 2192 (1955).
[11] J. L. Hoard and J. D. Stroupe *X-ray Crystal Structure of UF_6*, Cornell Report A-1296 (1944).
[12] B. Weinstock and R. H. Crist *J. Chem. Phys.* **16**, 436 (1948).

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desired time to separate the PuF_6 from the nonvolatile decomposition product by distillation through a break-seal. The residue was then dissolved and assayed by alpha counting. The amount of decomposition computed from this was corrected for the presence of hexavalent plutonium in the residue, the correction amounting to 1% for the shorter experiment and 15% for the longer one. The difficulty in removing PuF_6 completely is believed due to its occlusion in the decomposition product. Such an effect was particularly noticeable in the longer experiment, where the PuF_6 came off very slowly although there was a good vacuum in the system. Warming of the decomposition product caused more PuF_6 to be released in a burst and caused the solid to blow through the apparatus. In the longer experiment the amount of F_2 formed was also determined, and found to agree with the amount of decomposition product on the basis of a net decomposition of PuF_6 to $PuF_4 + F_2$. The experimental results are given in Table 1.

TABLE 1.—RADIATION DECOMPOSITION OF SOLID PuF_6

PuF_6 (initial) (millimoles)	Time (days)	PuF_4 (millimoles)	F_2 (millimoles)	Decomposition rate (% per day)
0·69	1·0	0·0105	—	1·5
0·98	6·9	0·097	0·099	1·5

From the decomposition rate for the solid of 1·5% per day and the assumption that substantially all of the alpha energy is absorbed by the solid, the average energy absorbed per PuF_6 molecule decomposition is 30 eV. This value is similar to the average energy-loss by alpha particles per ion-pair formation that has been observed for a wide variety of substances.[13] Such a result suggests that ion-pair formation in solid PuF_6 leads to decomposition without recombination. Clearly this statement is an oversimplification of the decomposition process, because a wide variety of ionized species is probably formed. For example, when WF_6 is examined mass-spectrometrically with 80 eV electrons,[14] all of the singly ionized species of W are observed in significant quantities from WF_5^+ to W^+ and doubly ionized species from WF_4^{++} to W^{++}. If similar species are formed due to the interaction of alpha particles with PuF_6, the presence of only PuF_4 in the decomposition product could be explained on the basis of reaction of PuF_6 (or F_2) with the compounds containing less fluorine than PuF_4 and a dissociation into PuF_4 and F_2 for the pentavalent ion.

In order to reduce the loss of PuF_6 due to radiation decomposition during storage, the PuF_6 was stored as vapour in nickel cylinders (Fig. 2). Under these conditions a fair fraction of the alpha-particle energy is absorbed by the walls of the container and does not contribute to the decomposition of PuF_6. The success of this procedure is quite evident from the values given in Table 2, where the decomposition rate of PuF_6 upon storage as vapour in the nickel cylinder is found to be reduced by a factor of 4 from the decomposition rate in the solid. The measurements in the nickel container were based on the change in PuF_6 pressure initially present, 23·0 mm Hg, to the final pressure of 21·4 mm Hg after separation from the F_2 produced.

[13] G. FRIEDLANDER and J. W. KENNEDY, Chap. 7 *Nuclear and Radiochemistry*, John Wiley and Sons, Inc., New York (1955).
[14] M. G. INGHRAM *Phys. Rev.* **70**, 653 (1946).

Also included in Table 2 are decomposition rates that are twenty-five times smaller than the rate in the solid. These were observed for PuF_6 in quartz tubes which were used for the study of the absorption spectrum of PuF_6. The amount of PuF_6 remaining in these tubes was determined from the vapour pressure[1] and measurements of the highest temperature at which solid PuF_6 could be condensed in the small Pyrex side arm used for filling.

TABLE 2.—RADIATION DECOMPOSITION OF PuF_6

State	Container	Total decomposition (%)	Average decomposition rate (% per day)	Time (days)	Calculated time (days)
Solid	Pyrex tube	—	1·5	—	—
Vapour	Nickel	23·5	0·35	67	75
Vapour	Small quartz cell	39·2	0·063	624	193
Vapour	Large quartz cell	32·5	0·060	542	—

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The last column of Table 2 gives the calculated time to produce the observed amount of decomposition in the vapour if no recombination of the ion pairs occurs. These calculations are based on the observed rate of 1·5% per day in the solid, on the calculated range of the alpha particles as a function of the pressure,[13] and on MUND'S equations for the fraction of the total ionization that occurs in the vapour.[15,16] The agreement is very good for the 67-day experiment in the nickel can, but a large discrepancy is obtained for the smaller quartz tube, the observed time being three times larger than the calculated. The calculation was not made for the larger quartz tube, where the discrepancy would be even greater.

The explanation for the very much smaller decomposition rates found for PuF_6 in the quartz cells as compared to the decomposition rate found for solid PuF_6 probably involves an activated recombination mechanism. An activated recombination mechanism is believed necessary because of the thermodynamic instability of PuF_6, which will be discussed. The apparent discrepancy between the measurement in the nickel container and those in the quartz cells could be explained on the following basis. The measurement on the nickel can, which was made after a rather short time (sixty-seven days), could be interpreted as the approach to a steady state, while that in the quartz cells, which were made after an extended period of time, could represent the steady-state conditions.

A qualitative demonstration of the failure of the solid decomposition to reach a steady state has been obtained from the magnetic susceptibility measurement to be described. In this experiment a 4-mm spherical quartz capsule was filled with PuF_6 and sealed off. The vapour volume was so small in this system that, on the basis of the solid decomposition rate of 1·5% per day, the increase in fluorine pressure was

[15] W. MUND *J. Phys. Chem.* **30**, 890 (1925).
[16] S. C. LIND, p. 94 *The Chemical Effects of Alpha Particles and Electrons*, The Chemical Catalog Co., Inc., New York (1928).

calculated to be 1 atm per day. After two days the experiment was discontinued and the capsule kept under water. It was finally found to have exploded after ten days. Thus in the solid, even at higher F_2 pressures, a recombination mechanism slowing down the decomposition rate does not appear to occur.

Photochemical and thermal decomposition of PuF_6 also show rather complete decomposition without evidence of a steady state. In these systems the primary dissociation product is not strongly activated as compared to the ionized species produced in the alpha-particle track.

The possibility of recombination of PuF_4 deposited on the walls of the nickel container with fluorine gas has been also tested for a short period of time. In this experiment 141 mm of F_2 and 5 mm of PuF_6 in the vapour were kept in contact with the decomposition product on the walls for one week. The amount of PuF_6 at the end of the experiment was the same as that at the beginning ($\pm 1{\cdot}4\%$), indicating that no recombination with the decomposition product occurred.

Magnetic Susceptibility

The magnetic susceptibility of solid PuF_6 has been measured at 81°K and 295°K by the Faraday method. The details of this experiment and a discussion of the results are given in another publication.[17] The molar susceptibility was found to be 170×10^{-6} at 295°K and 131×10^{-6} at 81°K. This small, relatively temperature-independent, susceptibility is to be compared with the strongly temperature-dependent values of $3000\text{–}4000 \times 10^{-6}$ found at room temperature for compounds that are isoelectronic with PuF_6 (U^{+4}, Np^{+5}, and $PuO_2)^{+2}$.[18,19] It seems likely that the two nonbonding electrons in PuF_6, unlike those in U^{+4}, Np^{+5}, and $PuO_2{}^{+2}$ compounds, form a ground-state configuration for the molecule which is nondegenerate even at room temperature.

Raman Spectrum and Infra-red Spectrum

An unsuccessful attempt to obtain the Raman spectrum of PuF_6 vapour and a successful measurement of the infra-red spectrum has been made. The details of this work are given elsewhere.[10] The molecular structure of PuF_6 is taken as a regular octahedron, point group O_h, because of the similarity of its infra-red spectrum with that of UF_6. The fundamental vibration frequencies of PuF_6 are given in Table 3, together with the frequencies for UF_6 and NpF_6 for comparison. The measurement of the Raman spectrum of PuF_6 failed because rapid photochemical decomposition of the PuF_6 occurred even at 5461 Å. In these experiments the PuF_6 initially at 2-atm pressure had decomposed by 50% after ten minutes of exposure. In a similar experiment with UF_6 vapour no decomposition was observed after a total exposure of seventy-two hours.[20]

Absorption Spectrum in Visible and Near-infra-red

The absorption spectrum of PuF_6 vapour has been investigated in collaboration with J. K. BRODY, F. S. TOMKINS, and M. S. FRED. The PuF_6 was contained in a

[17] D. M. GRUEN, J. G. MALM, and B. WEINSTOCK *J. Chem. Phys.* **24**, 905 (1956).
[18] D. M. GRUEN and C. A. HUTCHISON JUN. *J. Chem. Phys.* **22**, 386 (1954).
[19] J. K. DAWSON *Nucleonics* **10**, 39 (1952).
[20] H. H. CLAASSEN, B. WEINSTOCK, and J. G. MALM *J. Chem. Phys.* (to be published.)

quartz cell 10 cm in length at a pressure of 100 mm Hg. The spectrum was photographed over the region 5000–12,000 Å with a Jarrell-Ash spectrograph with a dispersion of 5 Å/mm and the Argonne 30-ft spectrograph with a dispersion of 1·8 Å/mm. In order to obtain sufficient absorption for the weaker bands, multiple traversal of the light through the cell was used, with the number of passes varying from one to eight. Below 4500 Å the absorption intensity increases greatly, and hence the photographic observations were limited to wavelengths greater than 5000 Å to avoid very rapid photochemical decomposition. Beyond 12,000 Å, the photographic limit in the infra-red, the spectrum was examined with a conventional infra-red spectrophotometer.

TABLE 3.—FUNDAMENTAL VIBRATION FREQUENCIES

Designation	Symmetry species	Spectral activity	Frequencies (cm^{-1})		
			UF_6	NpF_6	PuF_6
ν_1	a_{1g}	Raman, *p*	668	648	628
ν_2	e_g	Raman, *dp*	532	528	523
ν_3	f_{1u}	Infra-red	626*	624*	615*
ν_4	f_{1u}	Infra-red	189	200	203
ν_5	f_{2g}	Raman, *dp*	202	206	211
ν_6	f_{2u}	Inactive	144	164	171

* This is the only fundamental directly observed in the infra-red.

Over the range 5000–25,000 Å the spectrum consists of about six groups of bands, each group evidently corresponding to a different electronic transition as in the rare-earth spectra. Each group of bands consists of three or four bands of various intensities and separations. These separations are of the order of 100 Å and evidently form a vibrational spectrum that is superimposed on the electronic transition. The bands in these groups have a width of about 50 Å that is probably due to unresolved rotational structure, with the exception of one weak sharp band at 9371 Å. Some of the separations in individual bands recur from group to group. Under high dispersion, fine structure is found in many of the bands that consists of a great many sharp absorption lines, of which some are arranged in obvious sequences of about 10–15 cm^{-1} and others without obvious regularity. This structure is too fine to be due to vibrational lines and too coarse to be due to rotational lines. It is being investigated further in high orders of the 30-ft spectrograph.

Chemical Properties

A preliminary study of the chemical properties of PuF_6 has been made, particularly from the point of view of comparing its behaviour with that of UF_6. The vigorous hydrolysis of PuF_6 has already been mentioned, as well as the more stringent preparative procedure required compared to that for UF_6. The latter observation suggests that PuF_6 is much less stable than UF_6 toward dissociation into F_2 and a lower fluoride. This relative instability of PuF_6 has been more quantitatively demonstrated in several ways which will be described.

An interesting method for the processing of uranium reactor fuel rods has been reported by KATZ, HYMAN, and VOGEL,[21] in which uranium is converted into UF_6 by liquid BrF_3 at low temperature and volatilized away from the bulk of the fission products. The behaviour of plutonium in this system is of interest, and was investigated in collaboration with H. H. HYMAN and I. SHEFT by observing the interaction of PuF_6 with BrF_3. In this experiment, PuF_6 (45 mg) was distilled onto the surface of degassed BrF_3, which was frozen in a Fluorothene tube. As the BrF_3 was allowed to warm, the PuF_6 reacted rapidly at the surface and formed an insoluble precipitate. The mixture was then refluxed at 100°C for fifteen hours, and the BrF_3 finally distilled out. Analysis of the distillate for plutonium showed 0·1% (45 μg) of the original sample to be present. The residue in the Fluorothene tube accounted for the remainder of the plutonium used, and contained two solid phases. An X-ray pattern of one of these phases identified it as PuF_4; the other did not give an X-ray pattern, and was presumably amorphous. On the basis that the reaction proceeded in the manner

$$PuF_6 + BrF_3 = PuF_4 + BrF_5 \tag{1}$$

the equilibrium constant

$$K_p = \frac{(BrF_5)}{(PuF_6)(BrF_3)} \tag{2}$$

is 1000 atm^{-1} at 100°C. For this calculation the pressure of BrF_3 is taken at 1 atm and the relative concentration of BrF_5 and PuF_6 taken as the ratio of the initial amount of PuF_6 to the final amount found in the distillate.

The fluorination of BrF_3 to BrF_5 by PuF_6 demonstrated by this experiment occurs with greater rapidity than the corresponding reaction between BrF_3 and F_2.[22] The experiment showed further that PuF_6 must be much less stable toward dissociation than UF_6, since the latter can be quantitatively prepared by the use of BrF_3 as a fluorinating agent.[23] In the volatility process for uranium reactor fuel elements, using BrF_3 as the fluorinating agent at low temperatures,[21] a fairly complete separation of plutonium from uranium should therefore be expected.

The difference in thermal stability between UF_6 and PuF_6 has also been demonstrated by using PuF_6 as the fluorinating agent for the preparation of UF_6 from UF_4. In this experiment a quartz boat containing UF_4 (56 mg) was exposed to PuF_6 (56 mg, 35 mm Hg pressure) in a Pyrex system. The section of the apparatus containing the quartz boat was then heated for 20 min at 200°C and subsequently for 4 h at 225°C. The composition of the vapour was qualitatively examined at various times by condensing the material in a side arm and observing its colour. At the end of 20 min the condensate was still strongly coloured, indicating that PuF_6 was still present in substantial amount; after 50 min only a faint yellow colour remained, indicating that the PuF_6 was largely converted to UF_6; the condensate was white at the end of the experiment, and analysis of the vapour then showed 14·3 mg UF_6 and $7{\cdot}7 \times 10^{-5}$ mg PuF_6. The boat contained three differently coloured solids, which upon X-ray analysis gave the following results: pink compound, PuF_4; black and

[21] H. H. HYMAN, R. C. VOGEL, and J. J. KATZ, Geneva International Conference on Peaceful Uses of Atomic Energy, Paper No. 546 (1955).
[22] O. RUFF and W. MENZEL *Z. anorg. Chem.* **202**, 49 (1931).
[23] H. J. EMELEUS, A. G. MADDOCK, G. L. MILES, and A. G. SHARPE *J. Chem. Soc.* 1991 (1948).

greenish black compounds, U_2F_9. The course of the reaction is given by the equations

$$4UF_4 + PuF_6 = 2U_2F_9 + PuF_4 \quad (3)$$

$$U_2F_9 + 1{\cdot}5PuF_6 = 2UF_6 + 1{\cdot}5PuF_4. \quad (4)$$

The presence of U_2F_9 as the only solid uranium phase present under the conditions of this experiment is in agreement with the phase diagram for the uranium-fluorine system.[6] The equilibrium constant for reaction (4)

$$K_p = (UF_6)^2/(PuF_6)^{1{\cdot}5} \quad (5)$$

calculated from these experimental results is 10^7 $(atm)^{1/2}$ at 495°K. This value is believed to be much too small, since in the system used the rate of attainment of equilibrium was diffusion-controlled, and only a relatively short time was used for the experiment. However, the result clearly demonstrates the very large difference in stability between UF_6 and PuF_6.

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Two reactions have been examined as a promising system for determining the heat of dissociation of PuF_6 calorimetrically. They are

$$PuF_6 + 2PuF_3 = 3PuF_4 \quad (6)$$

$$F_2 + 2PuF_3 = 2PuF_4 \quad (7)$$

which yield by difference

$$PuF_6 = PuF_4 + F_2. \quad (8)$$

To investigate reaction (6), a quartz boat was loaded with 55·2 mg PuF_3 and exposed to PuF_6 vapour (138 mg, 85-mm pressure) in a Pyrex system. Some of the dark purple PuF_3 was observed to be converted to a light pink compound immediately on exposure to PuF_6 at room temperature. A calculation from the change in pressure showed that 10 mg of PuF_6 had reacted at once, and no further change in the extent of the reaction was observed after 16-h further exposure at room temperature. The system was subsequently heated for 1 h at 118°C, and an additional 18 mg PuF_6 was determined to have reacted. The change in weight of the boat and contents accounted for 26·3 mg of the reacted PuF_6, in agreement with the pressure measurements. This accounted for a conversion of 80% of the PuF_3 to PuF_4. A sample of the boat contents did not give an X-ray pattern at first, but after it had been heated in the sealed X-ray capillary for 16 h at 305°C, a pattern for PuF_4 (with a trace of PuF_3) was obtained. The presence of an oxidation state higher than the tetravalent in the boat material was not detected either by solubility measurement in neutral aqueous solution or by spectrophotometric examination of an acidic solution of the product.

The failure of reaction (6) to go to completion (even at 118°C) is probably due to the quality of the PuF_3 that was used. The reaction (7) between PuF_3 and F_2 had been observed by one of us to go to completion rapidly at room temperature. This reaction was then tested with the present batch of PuF_3 in a Pyrex system by exposing it to HF-free fluorine gas at 300-mm pressure and room temperature. A portion (61%) of the purple PuF_3 was again observed to be very rapidly converted to the light pink PuF_4. The pink solid did not give an X-ray pattern until it was heated for 12 h at 230°C in the X-ray capillary, and then it gave the PuF_4 pattern. An attempt to prepare a more reactive form of PuF_3 will be made by alternate oxidation and reduction of the PuF_3.

An experiment was done to examine the thermal decomposition of PuF_6 in a Pyrex system and to identify the decomposition product. Heating for 30 min at 208°C and PuF_6 pressure of 50 mm showed little if any decomposition product on the walls. Heating for 1 h at 280°C resulted in fairly complete decomposition. The decomposition product was deposited on the walls as red single crystals (1 mm in size) and identified as PuF_4 by X-ray analysis.

An attempt to form an intermediate fluoride between 4 and 6 was made at 70-mm pressure by exposing 88·4 mg PuF_4 to 100 mg PuF_6 in a Pyrex system. At room temperature no reaction occurred; after 1 h at 180–210°C, 27 mg of the PuF_6 decomposed, and 19·4 mg of this material was found in the boat, as determined by the increase in weight. X-ray analysis indicated that only PuF_4 was present in the boat at the end of the experiment. The failure to find an intermediate fluoride between 4 and 6 in this experiment is consistent with many other observations that have been made of the decomposition of PuF_6; however, the mechanism of decomposition through an intermediate oxidation state is not ruled out.

A 0·5% solution of PuF_6 in *n*-perfluoroheptane (C_7F_{16}) has been prepared with difficulty. The container used was a quartz cell, in which absorption spectra measurements were made. Although the flourocarbon sample used had been carefully purified and tested for complete fluorination, it reacted rapidly with PuF_6 in the glass system. It was felt that the reaction was due to some undetected C—H bonds remaining in the sample, which were fluorinated by the PuF_6 and produced HF. Separation of the HF produced then permitted a successful solution of PuF_6 in the now completely fluorinated fluorocarbon (C_7F_{16}).

Thermodynamic Stability

It has been suggested in the experiments previously described that PuF_6 is unstable with respect to dissociation into F_2 and PuF_4, as given by equation (8). A measurement of the equilibrium ratio of F_2 to PuF_6 for equation (8) has been made at 220°C with a mixture initially containing 5 mm of PuF_6 and 141 mm of F_2. The mixture was kept at this temperature for seven days in a seasoned nickel container, and then rapidly cooled to room temperature before analysis. Since the rate of thermal dissociation had been found to be slow at this temperature in observations made in Pyrex systems, the equilibrium concentrations were probably little affected by this quenching procedure. The ratio of F_2 to PuF_6 which gives the value of K_p for equation (8) was found to be $1{\cdot}86 \times 10^3$, indicating that the PuF_6 had substantially decomposed. The F_2 analysis was made by pressure measurement; the PuF_6 was separated from the F_2, sealed off in a Pyrex tube, hydrolysed, and assayed by alpha counting.

The values of the thermodynamic functions for equation (8) derived from this measurement are given in Table 4. The entropies and heat capacities of PuF_6 and F_2 were obtained from spectroscopic constants.[10, 24] The entropy and heat capacity of PuF_4 were obtained from those of UF_4[25] by assuming that their difference in entropy at room temperature and above is given by $R \ln 5/3 = 1{\cdot}01$ cal mole^{-1} deg^{-1}, which is the approximate difference in their magnetic entropy.

The thermodynamic instability of PuF_6 toward dissociation has the interesting

[24] G. M. MURPHY and J. E. VANCE *J. Chem. Phys.* **7**, 806 (1939).
[25] D. W. OSBORNE, E. F. WESTRUM, and H. L. LOHR *J. Amer. Chem. Soc.* **77**, 2737 (1955).

TABLE 4.—DISSOCIATION OF PuF_6

T (°K)	K_p	ΔF° (kcal mole^{-1})	ΔS° (cal mole^{-1} deg^{-1})	ΔH° (kcal mole^{-1})
493	$1{\cdot}86 \times 10^3$	−7·4	−0·4	−7·6
298	$3{\cdot}8 \times 10^5$	−7·6	−2·3	−8·3

consequence that it becomes more stable as the temperature is raised. This can be seen at once from the van't Hoff relation

$$\frac{d \ln K_p}{dT} = \frac{\Delta H^\circ}{RT^2} \tag{9}$$

and the fact that ΔH° is negative. This explains the results of many experimenters in the 1940's who observed that PuF_4 volatilized in a F_2 gas-stream at elevated temperatures, but then decomposed downstream. Their failure to collect PuF_6 was probably due to less-favourable equilibrium conditions downstream at lower temperatures resulting in rather complete dissociation of the PuF_6 that was formed at the higher temperatures.

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We have demonstrated the decrease of K_p with temperature by heating F_2 at 775-mm pressure for 2 h at 500°C in a nickel can in which PuF_4 was present on the walls but in which PuF_6 was not initially present. The experiment was ended by rapidly cooling the container and measuring the amount of PuF_6 that was produced in the manner previously described. We obtained 22·7 mg PuF_6 and a value of 440 for the ratio of F_2 to PuF_6 pressures. This value for K_p is smaller than that at 220°C, as predicted, but the true value of K_p at 500°C is undoubtedly even smaller, because a substantial change in the composition of the equilibrium mixture probably occurred while the reaction vessel was cooling, at least until it cooled below the temperature of 280°C. It is of interest to estimate the temperature to which this value of K_p, 440, corresponds. This is done by integrating equation (9) with the assumption that ΔH° is constant and equal to −7·6 kcal mole^{-1} and that K_p is equal to $1{\cdot}86 \times 10^3$ at 220°C. The temperature so obtained, 330°C, demonstrates that an appreciable change in the equilibrium concentration occurred during the cooling from 500°C.

The rapid equilibration of PuF_6 at temperatures above 280°C makes an experimental determination of the change of equilibrium constant of equation (8) with temperature very difficult. We therefore calculated the heat of dissociation by making use of heat capacity and entropy data combined with an equilibrium-constant measurement obtained at 220°C. In order to check the reliability of this procedure, we are in the process of determining the heat of reaction calorimetrically by the use of reactions (6) and (7).

It is a curious fact that in spite of its thermodynamic instability and reactivity, PuF_6 can be stored for long periods of time at room temperature with rather small decomposition. This is particularly evident in the examples of the quartz absorption cells which were described. Further experiments are planned in order to clarify our understanding of the thermal dissociation process.

Acknowledgements—The authors are particularly indebted to Dr. STANLEY SIEGEL for the many X-ray determinations that were made to identify the reaction products.

Acknowledgement is also made to Dr. J. C. HINDMAN for his help in interpreting the spectrophotometric data and in the attempts to identify an intermediate fluoride between +4 and +6; to RALPH BANE and MARY LOU RAUH for fluorine analyses; to JAMES H. PATTERSON, HAROLD EVANS, and ROBERT HORNBECK for plutonium analyses; to CHARLES M. STEVENS for mass spectrometer analyses; to LAURIDS ROSS for uranium analyses; to JOHN FARIS for spectrochemical analyses; and to STANLEY J. RYMAS and DALE HENDERSON for alpha-pulse analyses.

J. Inorg. Nucl. Chem., 1956, Vol. 2, pp. 395 to 402. Pergamon Press Ltd., London

THE CHLORIDE COMPLEXES OF TRIVALENT PLUTONIUM, AMERICIUM, AND CURIUM

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(*Received* 29 *November* 1955; *in final form* 30 *January* 1956)

Abstract—The dissociation constants of the monochloride complexes of trivalent plutonium, americium, and curium have been found to be identical in dilute hydrochloric-acid solutions, with a value of 0·068 corrected to zero ionic strength. In concentrated hydrochloric-acid solutions the relative complexing power has been shown to be plutonium $\geqslant$ americium $>$ curium. This result has been discussed with reference to a theory of *f*-orbital hybridization in the actinides.

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INTRODUCTION

THE absorption spectrum of trivalent plutonium chloride solutions is not appreciably affected by changes in the chloride ion concentration up to about 4 M, although noticeable differences are observed with tetra-and hexavalent plutonium under the same conditions.[1] From this it has been assumed by some authors that negligible complexing of trivalent plutonium with chloride occurs in dilute hydrochloric-acid solution. However, CONNICK and MCVEY[2] have drawn attention to the fact that the couple Pu^{3+}—PuO_2^{2+} has the same potential (−1·02 V) in hydrochloric-acid solution as in perchloric acid; since the hexavalent ion is believed to be complexed by the chloride ion, it would appear that the trivalent ion must be complexed too, to a similar extent. Furthermore, ion exchange work has shown that some separation of trivalent plutonium, americium, and curium occurs in chloride solution.[3] The potential and ion exchange behaviour both suggest that some complexing of plutonium occurs. The lack of supporting evidence from the absorption spectra is not important, since it is possible that complex formation can occur without distinct changes being produced in the spectra.

The relative complexing power of the trivalent ions of plutonium, americium, and curium is of interest because of the unusual behaviour of these ions when eluted from cation exchange columns by hydrochloric-acid solutions. DIAMOND *et al.*[3] have reported an unexpected reversal of elution order of these three elements on changing them from dilute to concentrated-acid systems.

EXPERIMENTAL

The dissociation constants were measured by an ion exchange method which is slightly modified from that described by SCHUBERT,[4] and SCHUBERT, RUSSELL, and MYERS.[5]

[1] J. C. HINDMAN and D. P. AMES, *The Transuranium Elements*, McGraw-Hill Book Co. Inc., New York 1949. Paper 4.2; and J. C. HINDMAN, *ibid.*, Paper 4.4.
[2] R. E. CONNICK and W. H. MCVEY, *J. Amer. Chem. Soc.*, **75**, 474 (1953).
[3] R. M DIAMOND, K. STREET, Jr., and G. T. SEABORG, *J. Amer Chem. Soc.*, **76**, 1461 (1954).
[4] J. SCHUBERT, *J. Phys. Colloid Chem.*, **52**, 340 (1948).
[5] J. SCHUBERT, E. R. RUSSELL, and L. S. MYERS, *J. Biol. Chem.*, **185**, 387 (1950).

For the dissociation reaction

$$MA_x^{(n-x)+} \rightleftarrows M^{n+} + xA^-$$

these authors derived the equation for the dissociation constant K

$$K = [A^-]^x/(K_d^0/K_d - 1) \tag{1}$$

where $[A^-]$ is the concentration of the complexing anion, K_d^0 is the distribution ratio when $[A^-] = 0$, and K_d is the ratio when $[A^-] \neq 0$.

The equation assumes that the positively charged complex ion $MA_x^{(n-x)+}$ does not undergo ion exchange. In order to allow for the exchange which must occur, SCHUBERT and LINDENBAUM[6] derived a correction factor f to be applied to the dissociation constant:

$$f = 1 - d/K_d \tag{2}$$

where d is the distribution ratio of the complex ion.

Their method of obtaining d was to assume that for a complex ion with one positive charge, the distribution ratio of another monopositive ion, sodium, could be used without introducing error. However, the affinity of an ion for a resin depends upon its hydrated radius as well as upon its charge, so a more fundamental method of obtaining d is required.

Application of the factor f to the dissociation constant equation (1) gives

$$K = [A^-]^x(K_d - d)/(K_d^0 - K_d) \tag{3}$$

Let these symbols now apply to one experiment where the concentration of a competing cation (e.g. the acidity of the solution) is given by $[H^+]$. In another experiment where the competing cation concentration is given by $[H_1^+]$ and the concentration of complexing anion $[A^-]$ is kept the same as before, the following equation can be written for the new dissociation constant at the different ionic strength:

$$K_1 = [A^-]^x(K_{d_1} - d_1)/(K_{d_1}^0 - K_{d_1}) \tag{4}$$

Now, for any ion-exchange reaction

$$M^{n+} + nHR \rightleftarrows MR_n + nH^+$$

where R signifies a cation resin, application of the law of mass action, using mole fractions for the resin phase, leads to the expression

$$K_{dM} \propto 1/[H^+]^n \tag{5}$$

(where K_{dM} is the distribution ratio for the ion M^{n+}), and when the concentration of M^{n+} is very small.

[6] J. SCHUBERT and A. LINDENBAUM, *J. Amer. Chem. Soc.*, **74**, 3529 (1952).

Therefore $$d_1 = d[H^+]^{n-x}/[H_1^+]^{n-x}$$

and substituting in equation (4) for d_1

$$K_1 = [A^-]^x\{K_{d_1} - d([H^+]/[H_1^+])^{n-x}\}/(K_{d_1}^0 - K_{d_1}) \quad (6)$$

In equations (3) and (6) there are three unknowns K, K_1, and d. If the two ionic strengths used (with the different amounts of competing cation) are not very different, and especially if they lie between 0·2 and 1, an approximate value for d can be obtained by assuming that $K = K_1$. Alternatively the ratio of K to K_1 can be obtained, if both ionic strengths are below 0·5, by applying DAVIES's[7] empirical formula for the calculation of activities from ionic strength.

Before determining the dissociation constants by this method, a preliminary experiment for each element was made at a fairly high ionic strength in order to determine whether complexes were formed, and if so, at what chloride-ion concentrations. For these experiments the distribution ratios of the three metal ions between a cation resin and solutions of fixed ionic strength containing varying amounts of chloride ion were measured, and plotted as $1/K_d$ against chloride-ion concentration or this concentration squared. According to equation (1), such a plot gives straight lines when the chloride-ion concentration is raised to a power equal to the number of ligands. The results plotted in Figs. 1 and 2 show that 1:1(MCl^{2+}) complexing occurs for all three elements and that some 1:2(MCl_2^+) complexing is occurring by the time the chloride concentration has reached 1 M. The graphs show that appreciable complexing occurs at 0·2 M chloride ion so the dissociation constants were measured at ionic strengths of 0·2 and 0·5 by determining the distribution ratios of the metal ions between Amberlite IR-120 and the various solutions described in the table. It was assumed that in perchlorate media no complexing occurred, and the distribution ratios determined in these solutions were used for the K_d^0 values in equation (1). The distribution ratios from the hydrochloric-acid solutions were used as K_d in the same equation, and the dissociation constants were calculated. The results at 0·2 M and 0·5 M acid (0·2 M chloride ion) were used to calculate d. However, this correction was found to be negligible. This is not unreasonable, since, at the low ionic strength used, the difference between the affinities of trivalent and divalent cations for a resin is very large. This difference rapidly decreases at higher ionic strengths, and the correction factor would then become significant.

The distribution ratios between an anion exchange resin Amberlite IRA-400 and concentrated hydrochloric-acid solutions for the three elements were of interest as a measure of the relative amounts of anionic complex (presumably MCl_4^-) formed in these solutions. The results are also given in the table.

The plutonium, americium, and curium used in this work were prepared as follows: A sample of plutonium was dissolved in hydrochloric acid and precipitated as hydroxide with ammonia. After being washed, the precipitate was dissolved in 2 M perchloric acid. Just before use, the solution was made 0·05 M with respect to hydriodic acid, to ensure the absence of tetravalent plutonium throughout the experiment.

A solution of americium in 5 M nitric acid was obtained from A.E.R.E., Harwell. It was assumed that the americium was in the trivalent state.

[7] C. S. DAVIES, *J. Chem. Soc.*, 2093 (1938).

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A solution of curium in 5 M nitric acid was obtained from A.E.R.E., Harwell. Just before use it was purified by extracting its α-active daughter 238-plutonium with an organic solvent.

Amberlite IR-120, grain size BS 52–100, was the cation resin used. It was prepared by washing thoroughly with dilute perchloric acid and then with water, and finally drying in air. The anion resin was Amberlite IRA-400, grain size BS 65–80, prepared by washing with dilute hydrochloric acid and water and then drying in air.

The distribution ratios were determined as follows. The perchlorate and chloride solutions of the correct concentration were prepared by diluting Analar reagents with water, and a small volume

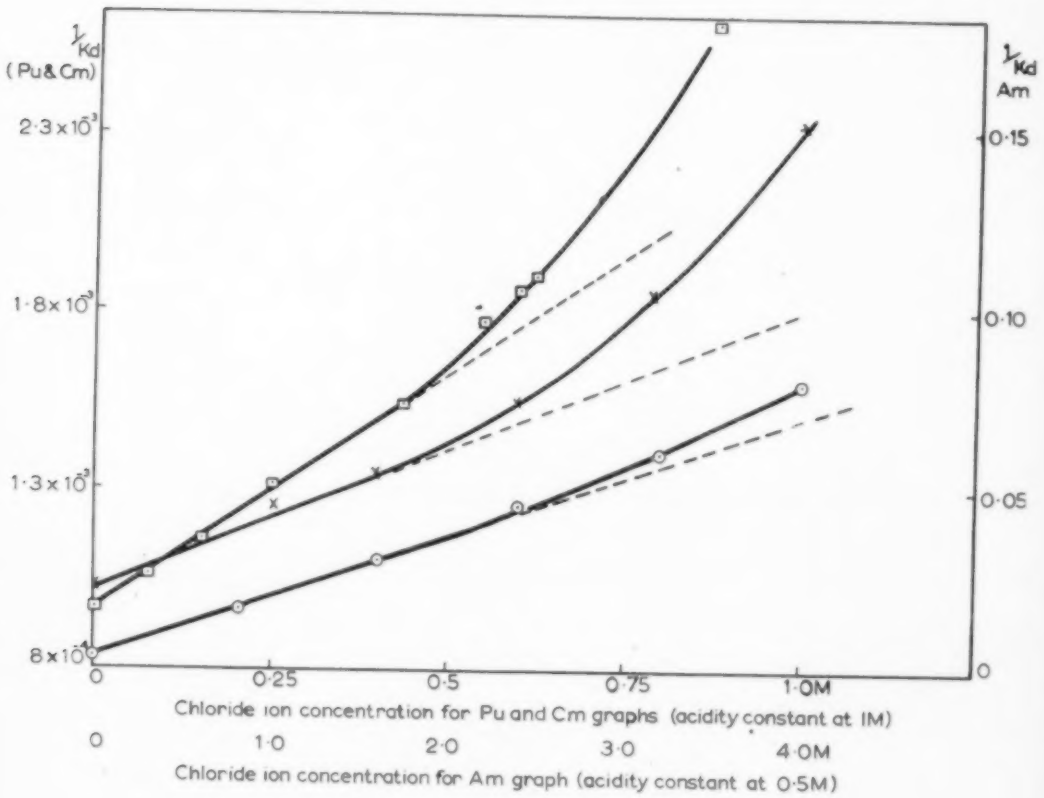

FIG. 1. ○ Plutonium
□ Americium
× Curium

(about 0·005 ml) of the plutonium, americium, or curium solution was added to each. 5-ml volumes in duplicate of these mixtures were shaken with known weights (50–150 mg) of the resin for several hours to reach equilibrium. (With the 0·2 M acid solutions it was necessary to shake for about 60 hours before equilibrium was obtained.) The concentrations of the plutonium, americium, or curium in the aqueous phase at equilibrium were determined by transferring aliquots to glass counting trays and measuring the alpha activity by means of scintillation counters. In solutions with a high salt content it was necessary to coprecipitate the activity on lanthanum fluoride for counting. Two methods were used for determining the concentrations in the resin phases: when the distribution ratio was high enough, the difference between the alpha activities of the solutions before and after shaking with the resin was used, but in other cases the resin at equilibrium was quickly washed with

water and then shaken with two small volumes of 10 M nitric acid to remove the activity from the resin for alpha assay as before.

The distribution ratio K_d is defined as α d.p.m. per g of resin/α d.p.m. per ml of solution

Some results are given in the table and others in graphical form (Figs. 1 and 2.)

The distribution ratios were used to calculate the dissociation constants for the reaction

$$MCl^{2+} \rightleftarrows M^{3+} + Cl^-$$

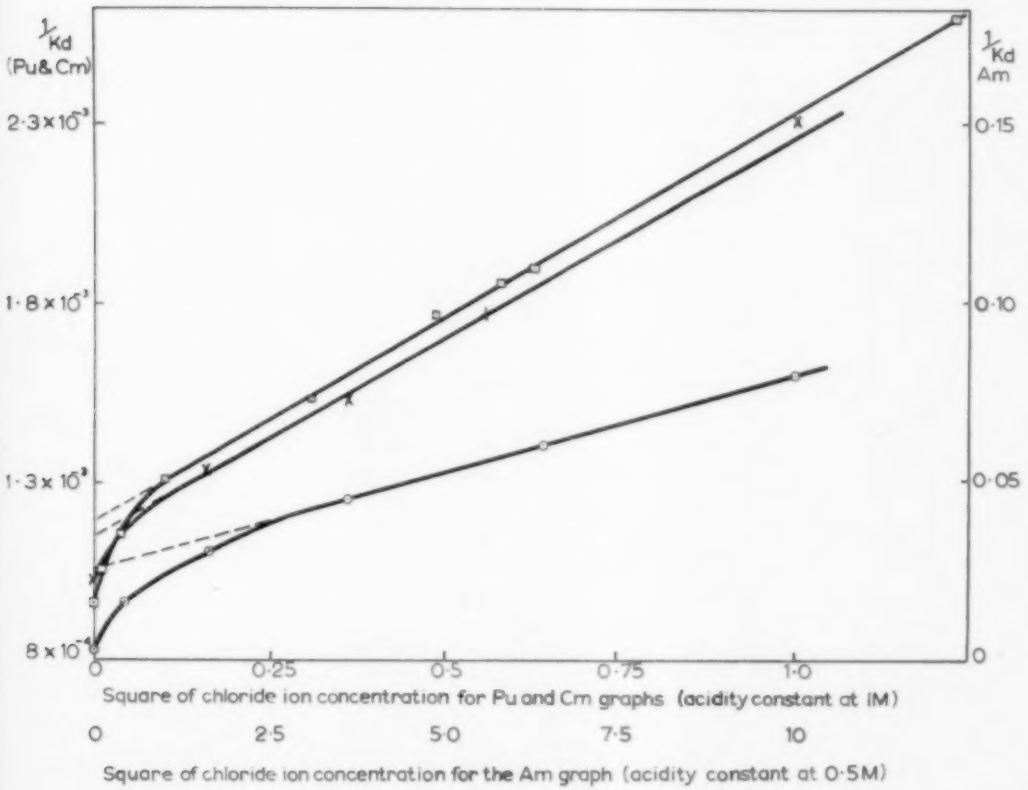

FIG. 2. ○ Plutonium
⊡ Americium
× Curium

The constants were corrected to zero ionic strength by application of the Davies empirical equation, to give the thermodynamic dissociation constants K_c. These values are also given in the table.

To confirm the large difference between the plutonium on one hand and the americium and curium on the other in 12·6 M hydrochloric acid, a simple ionic migration experiment was made in about 12 M hydrochloric acid in a conventional three-compartment apparatus. It was found that a mixture of initially Pu : Am : Cm = 1 : 2 : 2 produced a mixture of Pu : Am : Cm = 9 : 1 : 1 in the anode compartment.

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Resin	Element	Ionic strength	Chloride ion concentration	K_d	K_d^0	K	K_0
Cation	Pu	0·207	0·207	$1·54 \times 10^5$	$2·26 \times 10^5$	$0·44_3$	$0·067_7$
		0·5	0·5	$4·75 \times 10^3$	$8·86 \times 10^3$	0·58	0·065
		0·5	0·2	$6·53 \times 10^3$	$8·86 \times 10^3$	0·56	0·063
		1·0	1·0	$6·28 \times 10^2$	$1·20 \times 10^3$	1·1*	
	Am	0·206	0·206	$1·25 \times 10^5$	$1·83 \times 10^5$	$0·44_5$	$0·068_3$
		0·5	0·5	$5·46 \times 10^3$	$1·02 \times 10^4$	0·58	0·065
	Cm	0·195	0·195	$1·28 \times 10^5$	$1·86 \times 10^5$	$0·42_6$	$0·067_6$
		0·5	0·5	$5·44 \times 10^3$	$9·58 \times 10^3$	0·66	0·074
Anion	Pu	—	8	0·17			
			10	3·4			
			12·6	~470			
	Am	—	8	0·21			
			10	0·41			
			12·6	~0·42			
	Cm	—	8	0·19			
			10	0·36			
			12·6	~0·45			

* This value was calculated assuming only one complex species $PuCl^{2+}$ is formed.

DISCUSSION

It is now clear that trivalent plutonium does complex with chloride ions to an appreciable extent in 1 M hydrochloric acid. A value of 1·1 is obtained for the dissociation constant in this solution if it is assumed that only one complex species $PuCl^{2+}$ is present. This value is of the same order as those of 1·4 for the $LaCl^{2+}$ complex, measured by CONNICK and MATTERN,[8] and 0·6–0·7 for the $CeCl^{2+}$ complex, measured by CONNICK and MAYER.[9] Reference to Figs. 1 and 2 shows that some $PuCl_2^+$ may be present, and from Fig. 2 it is possible to calculate that the gross dissociation constant ($k_1 \cdot k_2$) is about 2. As far as is known, no quantitative data on chloride complexing of hexavalent plutonium have been reported, but from the results of CONNICK and MCVEY on the formal potential of the Pu^{3+}-PuO_2^{2+} couple, it is now possible to suggest that values similar to those given above for the trivalent ion are applicable.

By analogy with the lanthanides and from the known behaviour of the transcurium elements, the relative dissociation constants of the complex ions of plutonium, americium, and curium should decrease in that order. In dilute hydrochloric acid (0·2 M) the three constants have been found to be identical (0·068 corrected to zero ionic strength), while in concentrated hydrochloric acid solutions, the plutonium anionic complex must be considerably more stable than those of americium and curium. It was believed that tetravalent plutonium was absent in all experiments

[8] R. E. CONNICK and K. L. MATTERN. Unpublished work noted by CONNICK and MCVEY loc. cit.
[9] R. E. CONNICK and S. W. MAYER, *J. Amer. Chem. Soc.*, **73**, 1176 (1951).

owing to the presence of the hydriodic acid. These results therefore confirm the unexpected complexity of the hydrochloric-acid ion-exchange elution behaviour noted by DIAMOND *et al.*[3] and THOMPSON *et al.*[10] These authors also found that americium was eluted from cation resins before curium by very concentrated hydrochloric acid. It can therefore be assumed that americium is slightly more complexed by chloride ions than curium, even though the differences between them in the present work were hardly significant.

DIAMOND, STREET, and SEABORG suggested bond hybridization involving the 5*f* orbitals to explain the greater amount of chloride-ion complexing of the actinide elements as compared with the lanthanides. In the case of the actinides, the 5*f* orbitals either do not shrink as rapidly as the 4*f* or they have greater spatial extension relative to the corresponding *s*- and *p*-orbitals, to account for the greater availability of the 5*f* orbitals for hybrid bond formation.

If we consider the elements actinium to curium, as the atomic number *Z* increases, the 5*f* orbital changes from an "outer" function to a shielded "inner" function.[11] Between these two elements it passes through a region where the energies of the *f* and *d* electrons are very similar. Therefore the availability of the *f* orbitals for hybridization must increase to a maximum as *Z* increases and then decrease to a low value, as the orbitals shrink down to the ideal value for hybridization and then fall below it. It would be expected that this effect would show itself in increasing use of *f* electrons in bonds and increasing strengths of association complexes, followed by a decrease in both. In actinium, thorium, and protactinium there is very little evidence of any *f* orbital hybridization. With uranium, GLUECKAUF and MCKAY[12] have indicated a possible *f* orbital contribution to the unusually strong complexing with nitrate ions (which may have a different explanation) and also to the large number of bonds formed by the uranium atom in such complexes; with uranium, neptunium, and plutonium in the pentavalent and hexavalent states (oxygenated ions), the metal-oxygen bonds employ *f* orbitals,[13, 14] and their force-constants pass through a maximum at NpO_2^{2+}.[15] With higher values of *Z*, anion exchange results have now shown the relative strengths of the multichloride complexes to be plutonium $\gg$ americium $>$ curium, and suggest that the hybridization has passed its maximum and is decreasing, as predicted above, this decrease being big enough to overcome the opposite effect of the decreasing ionic size.

At curium, the *f* electrons are sufficiently shielded to prevent their use as valency electrons, but they may not be as completely shielded as the 4*f* electrons in the lanthanides, since curium is much more strongly complexed with chloride ions than gadolinium.[3] Beyond curium, DIAMOND, STREET, and SEABORG have suggested that the *f* orbitals become more available again to give stronger complexing as *Z* increases, but it is only necessary to postulate that the shielding of the *f* electrons in these elements does not increase, to allow the decrease in ionic size to account for the stronger complexing tendency.

[10] S. G. THOMPSON, B. G. HARVEY, G. R. CHOPPIN, and G. T. SEABORG, *J. Amer. Chem. Soc.*, **76**, 6229 (1954).
[11] M. GOEPPERT-MAYER, *Phys. Rev.*, **60**, 184 (1941).
[12] E. GLUECKAUF and H. A. C. MCKAY, *Nature*, **165**, 594 (1950).
[13] R. E. CONNICK and Z. Z. HUGUS, *J. Amer. Chem. Soc.*, **74**, 6012 (1952).
[14] J. C. EISENSTEIN and M. H. L. PRYCE, *Proc. Roy. Soc.*, **229A**, 20 (1955).
[15] L. H. JONES and R. A. PENNEMAN, *J. Chem. Phys.*, **21**, 542 (1953).

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Acknowledgements—The authors wish to thank Dr. J. MILSTED of A.E.R.E., Harwell, for the americium and curium used in this work. Thanks are also offered to the Managing Director, U.K. Atomic Energy Authority (I. G.) for permission to publish this paper.

J. Inorg. Nucl. Chem., 1956, Vol. 2, pp. 403 to 414. Pergamon Press Ltd., London

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EQUILIBRIUM STUDIES ON NATURAL ION-EXCHANGE MINERALS—I

CAESIUM AND STRONTIUM

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(*Received* 27 *January* 1956)

Abstract—The uptake of Cs^+ and Sr^{2+} ions has been studied on a Lower Greensand soil of good exchange properties; slight fixation of Cs^+ is observed, but not of Sr^{2+}. Isotherms have been obtained for the system Cs^+—Sr^{2+}—soil at two different ionic concentrations; from these a value of $9{\cdot}3 \times 10^{-4}$ has been derived for the thermodynamic equilibrium constant of the exchange reaction

$$2CsX + Sr^{2+} \rightleftharpoons SrX_2 + 2Cs^+$$

where X represents the exchange complex within the soil. Other relevant thermodynamic data have been calculated for this system, and the results are compared with those of other workers on the pure clay mineral montmorillonite.

THE ion-exchange properties of soils are of fundamental importance in plant nutrition and for purposes of liming and fertilization, and have been studied for over a century since their importance was first realized.[1] They have been traced in large part to the presence of clay minerals within the soil complex.[2] In clays, the negative charges arising from the replacement of Si^{IV} by Al^{III}, and of Al^{III} by Mg^{II}, are balanced by the presence of positive ions such as Ca^{2+}, and to a lesser extent Na^+, K^+, Mg^{2+}, and other ions. The ion-exchange properties of soils and clays arise from the exchange of these ions with ions present in the solution with which the material is in contact. The cation-exchange capacities of clays vary enormously, from <10 milliequivalents (meq)/100 g for kaolinite to >100 meq/100 g for certain montmorillonites, other clays having intermediate values; soils will possess a capacity depending upon the type and amount of clay mineral which they contain, and in addition may possess additional capacity arising from the presence of other mineral constituents and of organic matter. For a full discussion of the mechanism of ion exchange in clays, reference should be made to standard texts on the subject.[3]

It has been suggested[4] that use should be made of the high capacity of montmorillonite for treatment of the highly active fission-product wastes arising from the processing of irradiated nuclear fuels. A logical extension of this approach is to consider the use which might be made of natural soils for similar purposes.[5] The latter case is also of interest in assessing the likely fate of active material which may be deposited on the soil as a result of accidental contamination. It was therefore decided to investigate the behaviour of certain typical fission products in relation to soils likely to be useful for such purposes; the present paper deals with caesium and strontium.

[1] THOMPSON, *J. Roy. Agr. Coll. Engl.* **11**, 68 (1850); WAY, *ibid.*, p. 313.
[2] KELLEY, "Cation Exchange in Soils", Reinhold, New York, (1948).
[3] GRIM, "Clay Mineralogy", McGraw-Hill, New York, ch. 7 (1953).
[4] HATCH, *American Scientist* **41**, 410 (1953); GINELL, MARTIN, and HATCH, *Nucleonics* **12** (12), 14 (1954).
[5] AMPHLETT, *Research* **8**, 355 (1955).

EXPERIMENTAL

Characterization and treatment of the soil. The soil used in these experiments was a Lower Greensand soil from Nuneham Courtenay, Oxon, which was known to possess good exchange properties. The natural soil, which possessed varying amounts of coarse, pebbly matter, was sieved to −40 mesh after air-drying; approximately 1 kg of sieved material was then thoroughly mixed for use in the experiments. Although natural soils are far from homogeneous, the good agreement between results obtained with different samples suggests that mixing was efficient and that representative results were obtained.

The soil sample thus prepared gave a slightly acid reaction (pH 5·5–6·0), and contained very little organic matter, so that its cation exchange capacity should be largely due to its clay mineral content; the capacity was determined with 1 N ammonium acetate at pH 7 and found to be 30·7 meq/100 g. X-ray examination of the clay fraction (particle size $< 2\ \mu$) showed the principal clay minerals to be montmorillonite and illite, together with a little kaolinite and other minerals.

Uptake experiments. The uptake of Cs and of Sr on natural soils, and the displacement of one of these ions by the other, was followed by means of experiments using small columns packed with soil. An accurately weighed quantity of soil, usually 1–3 g, was slurried with tap-water into a weighed 1-cm diameter glass column plugged at the lower end with glass-wool. After draining, the wet column was weighed, and the pore space within the column determined from the increase in weight and from the weight of soil taken, assuming unit density for the liquid within the pores. This method is only approximate, since it neglects the change in swelling for different salt solutions and also the change in weight when one ion is replaced by another. However, provided the pore space makes only a small contribution to the overall volume of liquid passed on saturating the column (as will be the case for appreciable capacities), errors in pore-space determination will affect only slightly the overall accuracy of the results. In work on montmorillonite with the mixed system ($Cs^+ + Sr^{2+}$) it has been found possible,[6] by labelling both species and estimating them individually, to derive a more satisfactory value for the pore space; this method was found to give values in good agreement with those obtained by the simpler method.

After preparation of the column, a solution of the species being investigated, labelled with a suitable tracer, was allowed to percolate slowly down the column under a head of several centimetres, giving a flow-rate of 8–12 ml/h. Samples of approximately 2 ml were collected in measuring cylinders, their volumes were noted, and 1·0-ml aliquots were counted under reproducible conditions with a standard Geiger-Müller tube and counting equipment; 1·0-ml samples of the original solution were also counted. Curves were drawn of effluent concentration (in meq/ml) against effluent volume (ml/g soil), the latter being plotted at the mid-points of samples; the uptake was estimated from the area over the breakthrough curves, corrected for the pore space. Displacement runs were made on active columns with inactive solutions of the same concentration as that originally used to saturate the column, and were continued until the effluent was of negligible specific activity. In many cases mass balances were checked between material on the column, total material used, and that in the effluent.

Cs^+ solutions were prepared by dissolving known weights of dried AR $CsNO_3$ in distilled water and adding suitable amounts of tracer ^{137}Cs as nitrate solution (supplied by the Radiochemical Centre, Amersham); the final pH of the solution was adjusted by adding acid or CsOH solution, a small correction being applied for the added Cs^+ ion in the latter case. Sr^{2+} solutions were prepared from $SrCO_3$ which had been irradiated in B.E.P.O. at Harwell to produce ^{89}Sr; this was dissolved in dilute nitric acid and the pH adjusted by the addition of acid or of inactive $SrCO_3$. ^{90}Sr is unsuitable as a tracer because of the activity of its daughter-product ^{90}Y, which in the absence of carrier yttrium will give a spuriously high reduction in the activity of the effluent.

RESULTS

Typical uptake curves for Cs^+ and Sr^{2+} are shown in Fig. 1; in general, there is a fairly sharp breakthrough followed by a smooth sigmoid curve trailing towards saturation; stepped curves were occasionally obtained, but were usually traceable to disturbances during the run. Variations in slope and shape between different

[6] GAINES, Thesis, Yale, 1954; *J. Phys. Coll. Chem.*, in course of publication.

breakthrough curves are probably due to heterogeneity of individual samples as regards particle size, and in this respect the kinetics will be far from ideal; despite this, however, agreement between different values of the exchange capacity was good.

Mass balance tests showed agreement to within 2%, except in one case where it

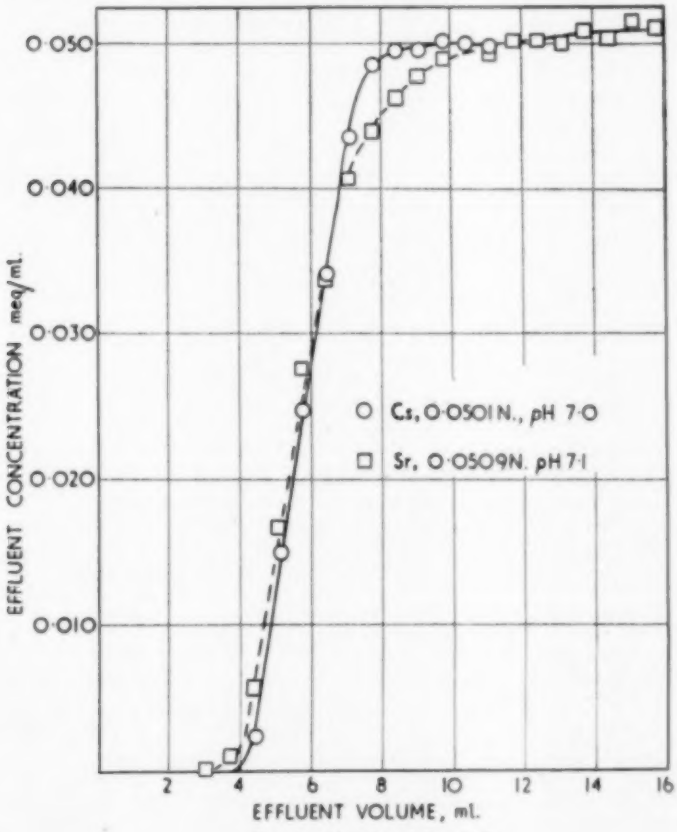

FIG. 1.—Uptake of Cs and Sr.

exceeded 4%. Since samples were counted for a sufficient number of counts to give a statistical accuracy of ~1%, and since the errors in planimetry and in estimating the volumes will be no greater than this, it is likely that the major sources of error arise from (a) difficulty in estimating the shape of the curve over the trailing portion, and (b) retention of activity within the measuring cylinders after emptying and rinsing out to make up to a standard volume for estimation of the total eluate specific activity. It is noteworthy that the total specific activity summed from the curve and from the eluate was always less than that of the original solution, and that it was found possible to remove activity from the cylinders on further rinsing with chromic acid. It is expected that the individual values of exchange capacity are correct to better than ±5%; comparison of the whole series suggests that the bulk soil-exchange capacity may be expressed to an accuracy of ~7%, which accords with the results of determinations made by other methods.

Apart from three high values, the pore space per gram of soil is reasonably constant at 0·60–0·80 cm^3/g, 60% of the values lying between 0·72 and 0·80 out of a total of twenty-four determinations; this suggests a fairly uniform degree of packing and of particle-size distribution. In one experiment the effect on pore space of substituting one cation for another was measured, with the following results:

Increase in weight of dry column after percolation of tap-water	= 2·0746 g
Increase in weight of dry column after saturation with $CsNO_3$ solution	= 2·1311 g
Weight increase due to replacement of Ca^{2+} by Cs^+	= 56·5 mg.

From the known exchange capacity of the soil, the expected weight increase when Cs^+ replaces Ca^{2+} is 67·9 mg; the variation in pore-space weight when Cs^+ replaces Ca^{2+} is therefore no greater than 12 mg in a total of ~2·0 g.

Uptake of Caesium and Strontium Individually

Eleven determinations of Cs-uptake were made, and five of Sr-uptake, the solution concentration varying from 0·02 to 0·05 N, and the pH from 1·4 to 8·8; the variation in exchange capacity with pH is shown in Fig. 2. Caesium-exchange capacities were determined on natural soil, on soil which had been converted to the Sr form, and also by isotopic exchange on inactive soil in the Cs form. The capacity for Cs is approximately constant above pH 3·5, and decreases rapidly below this value; uptake of Sr is more critically dependent upon pH, and for satisfactory removal of this element the pH should be above 5. Other workers[7, 8] have also found that in the case of Sr both the initial uptake and the saturation capacity are strongly pH-dependent, much more so than in the case of Cs. The mean value of the cation-exchange capacity derived from the Cs results is 27·3 ± 2 meq/100 g, while that from the complete series of experiments with Cs and Sr is 27·1 ± 2, compared with the value of 30·7 obtained with NH_4OAc.

Although the whole of the strontium exchanged on the soil may be displaced by treatment with a salt solution, it was never found possible to displace caesium completely in this way. Thus, if a soil saturated with tracer-active Cs were treated with an inactive Cs solution until the effluent possessed negligible specific activity, further treatment with dilute acid (3–6 N HNO_3) removed additional activity corresponding to 1–2% of the amount originally on the column. The activity removed by dilute acid gave an aluminium absorption curve identical with that of ^{137}Cs, showing that it was not due to an impurity in the original material, and blank experiments showed that the activity adsorbed on the glass was negligible. The removal of Cs^+ by acid appears to indicate that the ion is "fixed" to a slight extent upon this soil, i.e. that it is rendered relatively nonexchangeable towards ions other than the H^+ ion. Potassium fixation is a well-known phenomenon in soil chemistry, and both rubidium and caesium are fixed appreciably on the clay mineral vermiculite.[9] The isotopic exchange of Cs on montmorillonite is completely reversible,[10] but in view of the structural similarity

[7] SEEDHOUSE, unpublished results.
[8] BROCKETT and PLACAK, Proceedings of the 8th Industrial Waste Conference, Purdue University, 1953.
[9] BARSHAD, *Amer. Miner.* **33**, 655 (1948); **34**, 675, 1949.
[10] FAUCHER, SOUTHWORTH, and THOMAS, *J. Chem. Phys.* **20**, 157 (1952).

between vermiculite and illite some fixation on the illite fraction of the present soil is not unlikely.[11]

In the experiment in which traced Cs^+ ion was exchanged on an inactive Cs soil, the activity subsequently removed by acid was appreciably less than in the other runs; this would be expected, since the "fixed" Cs will largely be that derived from the original treatment with inactive solution, so that the traced Cs subsequently taken up should be almost completely exchangeable.

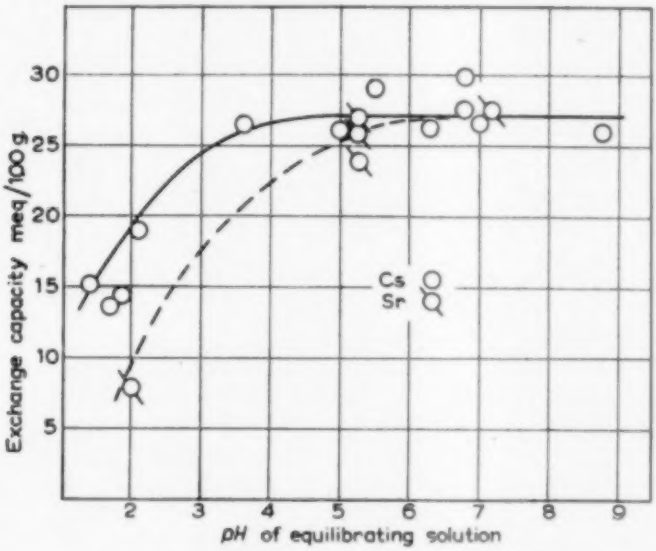

FIG. 2.—Exchange capacity as a function of pH.

The Mixed System Cs—Sr—Soil

Elution and displacement experiments showed that Cs was more strongly held on the soil than Sr, and isotherms for the system were derived in two ways.

(a) *Elution technique.* A sample of soil was saturated with tracer-active Cs and the capacity determined from the breakthrough curve in the usual manner. Caesium was then eluted with an inactive Sr solution of the same concentration as the original Cs solution, giving an elution curve with a trailing rear boundary (Fig. 3). GLUECKAUF has shown [12] that it is possible to derive the isotherm from such a curve by means of the expression

$$\frac{q}{q_0} = \left\{\frac{u}{C_0} + (V - V_0)\cdot\frac{C}{C_0}\right\}\cdot\frac{C_0}{q_0 x}$$

where q = capacity of exchanger for one species present at concentration C; in the present case q and C refer to Cs,

q_0 = total capacity at concentration C_0 (= total concentration),

u = area under elution curve from the value of C/C_0 chosen to complete elution,

V = volume of eluting solution corresponding to the value of C/C_0 chosen,

V_0 = pore-space volume,

and x = mass of exchanger.

[11] DR. R. K. SCHOFIELD, private communication.
[12] GLUECKAUF, *J. Chem. Soc.* 3282 (1949).

Values of V corresponding to different values of C/C_0 were taken from Fig. 3, all being normalized to one g of soil; q_0 was taken as the value determined by Cs uptake. Values of u were taken to an arbitrary point and corrected for the difference between the measured capacity to this point and the known total capacity; this avoided

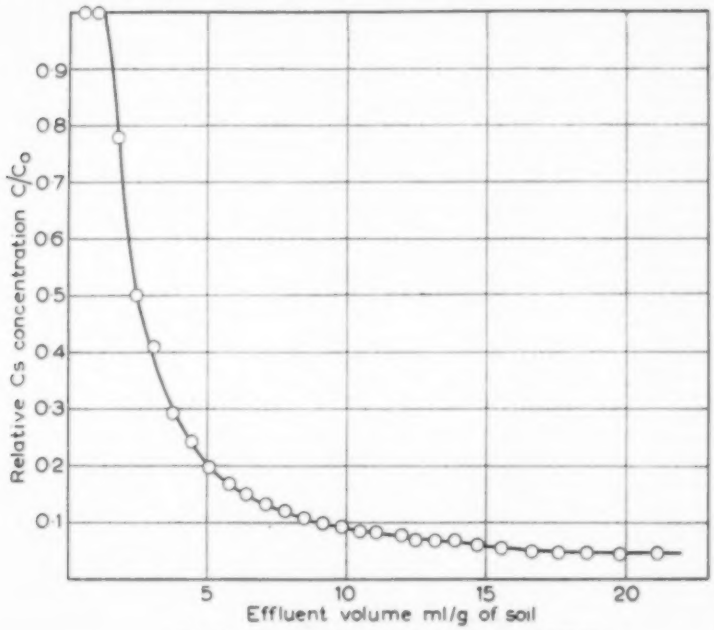

FIG. 3.—Elution of Cs^+ by Sr^{2+}. $Sr^{2+} = 0{\cdot}050$ N.

pursuing the trailing rear boundary to complete elution. The isotherm obtained in this way is given in Fig. 5.

(b) *Equilibrium technique*. The derivation of isotherms from elution data depends on the assumption that at all points on the elution curve the system is in complete equilibrium. It has been shown[10] that this is not so in the case of montmorillonite, and a method has been developed by which isotherms obtained from elution curves may be corrected on the basis of results of isotopic exchange experiments, where the deviations from equilibrium are readily calculated. Another disadvantage in the derivation of isotherms from elution data is that the accuracy is poor at low values of C/C_0, since V and V_0 are then comparable in size; since at low values of C/C_0 the isotherm is most steeply curved, considerable errors may arise in deriving thermodynamic data by integration over the complete isotherm. For these reasons it is preferable to carry out a series of equilibrations with solutions of the same total concentration C_0 and of varying relative Cs concentration C/C_0, determining values of q/q_0 in individual experiments. If both ions are traced, then q and $(q_0 - q)$ may be determined independently, either by chemical separation or by absorption experiments; an unequivocal determination of the pore space is also possible in this case.[6] In the present work we have traced only one ion, viz. Cs. Values of q were obtained by integration over the breakthrough curves; we feel that in view of the possibility of variations between different samples of soil, this gives a better check on the reliability

of individual runs than the method used by THOMAS in the case of montmorillonite, viz. to saturate the clay, displace the traced ions with an inactive salt solution, and count an aliquot of the eluate.

In this way a series of uptake curves was obtained at different values of C/C_0, for

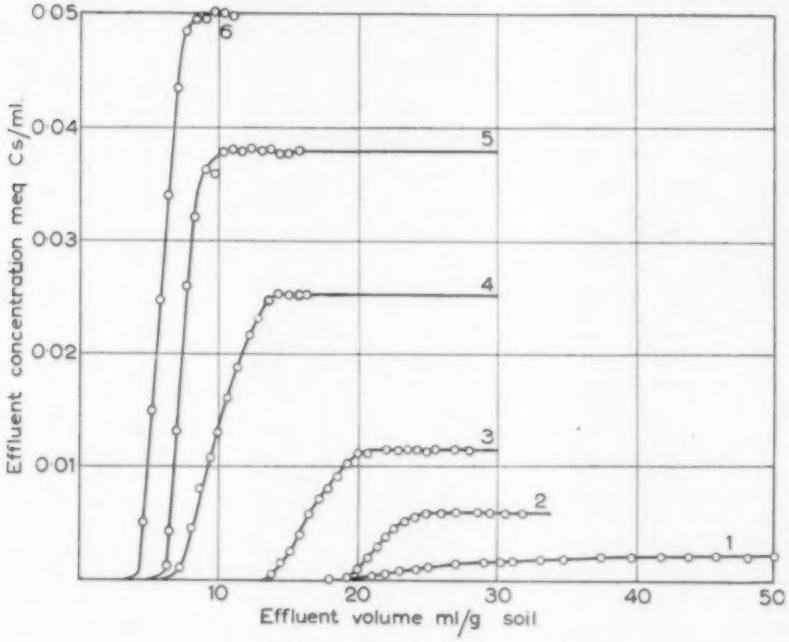

FIG. 4.—Uptake of Cs in presence of Sr.
C_0 = 0·05 N.
C/C_0 = 0·046 (curve 1), 0·126 (curve 2), 0·234 (curve 3), 0·500 (curve 4), 0·759 (curve 5), 1·000 (curve 6)

TABLE 1.—RELATIVE CONCENTRATION IN SOLID AND SOLUTION PHASE
(from equilibrium experiments)

Run	Total concentration C_0, meq/ml	Cs concentration C, meq/ml	Cs uptake q, meq/100 g.	C/C_0	q/q_0*
15	0·0200	$0·0019_5$	7·9	0·097	0·29
13	0·0200	$0·0049_6$	14·6	0·249	0·54
12	0·0201	$0·0101_4$	20·5	0·506	0·76
14	0·0201	$0·0150_8$	24·3	0·752	0·89
26	0·0501	$0·0023_2$	6·5	0·046	0·24
25	0·0501	$0·0063_1$	14·0	0·126	0·52
21	0·0494	$0·0115_7$	18·6	0·234	0·68
18	0·0500	$0·0250_2$	23·0	0·500	0·84
24	0·0500	$0·0380_2$	25·6	0·761	0·94

* Based on q_0 = 27·1 meq/100 g.

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$C_0 = 0{\cdot}02$ and $0{\cdot}05$ N; Fig. 4 shows the curves for $C_0 = 0{\cdot}05$ N, and values of q/q_0 as a function of C/C_0 are given in Table 1. The isotherms are plotted in Fig. 5, together with those for the system Cs—Sr—montmorillonite.[6] The value of q_0 used in these determinations is the mean value of 27·1 meq/100 g referred to above.

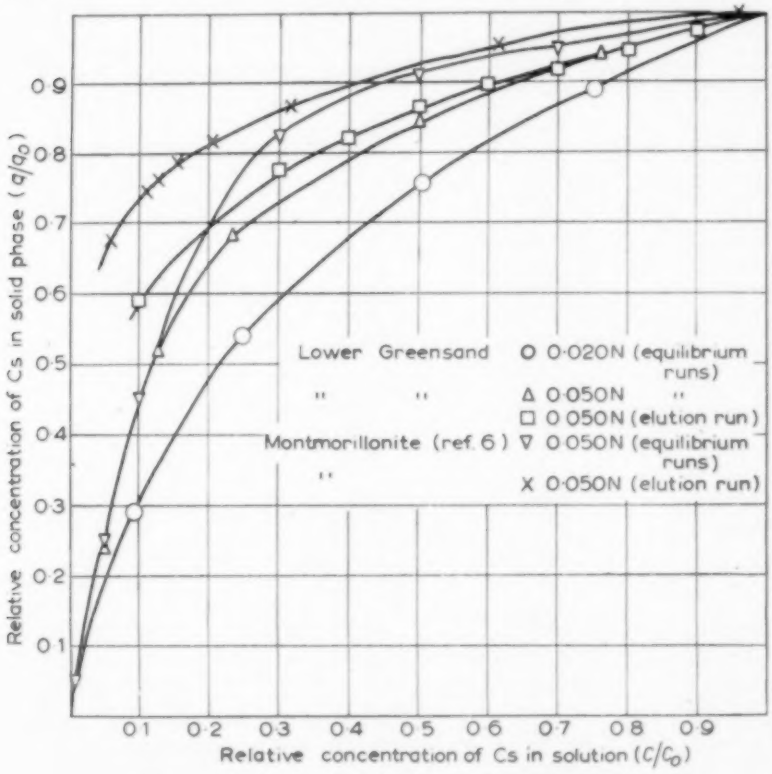

FIG. 5.—The Cs-Sr isotherm on Lower Greensand.

Comparison of the elution and the equilibrium isotherms at 0·05 N total concentration shows that the error involved in the former is 5% or less from $C/C_0 \simeq 0{\cdot}3$ onwards, rising rapidly below this value to ~30% at $C/C_0 = 0{\cdot}1$; since the isotherm over the range $C/C_0 = 0{\cdot}3$–$1{\cdot}0$ only covers a range of 0·73–1·0 in q/q_0, considerable errors would arise in deriving data from the whole of the elution isotherm. The discrepancy between the two isotherms is much less than in the case of montmorillonite, presumably because of the much higher flow-rates used in the latter work.

DISCUSSION

The isotherms for montmorillonite and for the soil are not greatly different, and in fact are coincident up to a value of $C/C_0 \simeq 0{\cdot}12$. If we consider the soil as possessing two kinds of exchange centres, viz. those of montmorillonite and those of illite, then the smoothness of the uptake curves and of the elution curves indicates that the system is behaving as a pseudohomogeneous exchanger, i.e. that the rates of exchange at the two centres are similar, even though the saturation capacities

differ greatly. If there were a considerable difference in uptake rate for the two types we would expect irregular curves, unless the flow-rate were sufficiently low to ensure equilibration with the centre having the lower exchange rate. It is perhaps fortunate that in this work the flow-rates have been low, and that the clay fraction of the soil is predominantly montmorillonite and illite, both of which exchange relatively slowly, while kaolinite exchanges much more rapidly.[3] It would appear that up to a value of $q/q_0 \simeq 0{\cdot}5$ (corresponding to $C/C_0 \simeq 0{\cdot}12$), exchange on the montmorillonite centres predominates; above this value, exchange on the soil favours Sr more than on the pure clay, although the overall effect is still to favour Cs relative to Sr. It seems reasonable to infer that this effect is due to the presence of illite in the soil, and that the negative free-energy change in the exchange

$$\text{Cs clay} + \text{Sr}^{2+} \rightarrow \text{Cs}^{+} + \text{Sr clay}$$

is greater for illite than for montmorillonite. Since the saturation capacities of illite and montmorillonite are so widely different (assuming rough values of 100 and 20 meq/100 g respectively, saturation of a 50% mixed clay would result in 83% of the ions being exchanged on montmorillonite) we must assume that the difference between the equilibrium constants for exchange on montmorillonite and on illite is quite large.

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The Equilibrium Constants

If we denote the clay by X, we may write the exchange equilibrium involving Cs and Sr as follows:

$$\begin{array}{ccccc} 2\text{Cs}X & + & \text{Sr}^{2+} & \rightleftharpoons 2\text{Cs}^{+} & + & \text{Sr}X_2 \\ q & & (C_0 - C) & C & & (q_0 - q) \end{array}$$

C and $(C_0 - C)$ are the concentrations of Cs^+ and Sr^{2+} ions in solution in equilibrium at total concentration C_0 with a clay containing q and $(q_0 - q)$ meq per unit weight of Cs and Sr respectively, the total cation-exchange capacity of the clay being q_0. If concentrations in solution and in the solid phase are expressed as fractions of C_0 and of q_0 respectively, the thermodynamic equilibrium constant may be written as

$$K = K_c' \cdot \frac{\gamma_{\text{Cs}}^2}{\gamma_{\text{Sr}}} \cdot \frac{f_{\text{Sr}}}{f_{\text{Cs}}^2}, \qquad (1)$$

where K_c' is the apparent equilibrium constant derived from the observed concentrations, γ is the ionic activity coefficient in solution, and f that in the solid phase. K_c' is given by the expression

$$K_c' = C_0 \cdot \frac{(1 - q/q_0)(C/C_0)^2}{(q/q_0)^2(1 - C/C_0)}, \qquad (2)$$

and in addition we have the relationships

$$K = K_c \cdot \frac{f_{\text{Sr}}}{f_{\text{Cs}}^2} \quad \text{and} \quad K_c = K_c' \cdot \frac{\gamma_{\text{Cs}}^2}{\gamma_{\text{Sr}}}. \qquad (3)$$

It will be noted that K_c' is dependent upon the *total* concentration C_0; this is always observed in exchange involving ions of different valency, and results in exchange

favouring the ion of lower valency at higher total concentrations, as will be seen from the isotherms in Fig. 5.

GAINES and THOMAS[6, 13] have recently given a comprehensive treatment of the thermodynamics of ion-exchange systems, in which the equilibrium constant K for a 1 : 2-valent system such as the present one is given by the expression

$$\ln K = -1 + \ln \frac{f_{Sr}(A)}{f_{Cs}^2(B)} + \int_0^1 \ln K_c \, . \, d\left(\frac{q}{q_0}\right) - 2\int_A^B N_s \, . \, d \ln a_s, \qquad (4)$$

where the integration is carried out at constant total normality (C_0 constant). A represents pure Sr clay in equilibrium with Sr^{2+} solution; B is pure Cs clay in equilibrium with Cs solution. N_s is the water content of the clay in moles per exchange equivalent, and a_s the water activity. In the absence of data concerning the relevant activity coefficients, it is customary to make certain approximations as follows:

(i) $f_{Sr}(A) = f_{Cs}(B) = 1$, i.e. the activity coefficients of Sr and Cs in the pure mono-ion clays in equilibrium with dilute solutions of the respective ions are unity; this is equivalent to assuming a negligible change in the water activity of the clay from infinite dilution to the salt concentration employed.

(ii) $\gamma_{Cs}^2/\gamma_{Sr} = 1$, i.e. $K_c = K_c'$. Although this is not strictly true, the error involved should not be large, and in the absence of data for activity coefficients in mixed salt solutions, the approximation is justified. Equation (4) then becomes

$$\ln K \approx -1 + \int_0^1 \ln K_c' \, . \, d\left(\frac{q}{q_0}\right) - 2\int_A^B N_s \, . \, d \ln a_s. \qquad (5)$$

In the absence of data for the water activity of clays, the second integral is neglected, giving an expression identical with that derived earlier by BONNER *et al.*[14]

Fig. 6 shows the variation in $\ln K_c'$ with q/q_0, values of K_c' being calculated from Fig. 5. Since estimation of K_c' is difficult at the ends of the isotherm, the values corresponding to $q/q_0 = 0$ and 1 were calculated from the limiting slopes of the isotherm at these points. If S is the slope, then it may be shown[6] that

$$\lim_{C \to 0} (\ln K_c') = \ln C_0 - 2 \ln S \qquad (6)$$

Fig. 6. also gives the curve for montmorillonite,[6] and the values of K are given in Table 2.

The constants for montmorillonite and for the soil are of the same order of magnitude, although the soil favours Sr uptake more than does the clay. The very small change in $\ln K$ over a concentration range of 0·02–0·05 N may indicate that the water-activity term in equation (5) is unimportant under these conditions, or it may be due to compensating factors involving the other terms. Within the accuracy of these experiments we may state that K, as determined above, is constant over this range of concentration.

Activity Coefficients in the Solid Phase

By extending the treatment above it may be shown[6, 13] that for any value of

[13] GAINES and THOMAS, *J. Chem. Phys.* **21**, 714, (1953).
[14] BONNER, ARGERSINGER, and DAVIDSON, *J. Amer. Chem. Soc.* **74**, 1044 (1952).

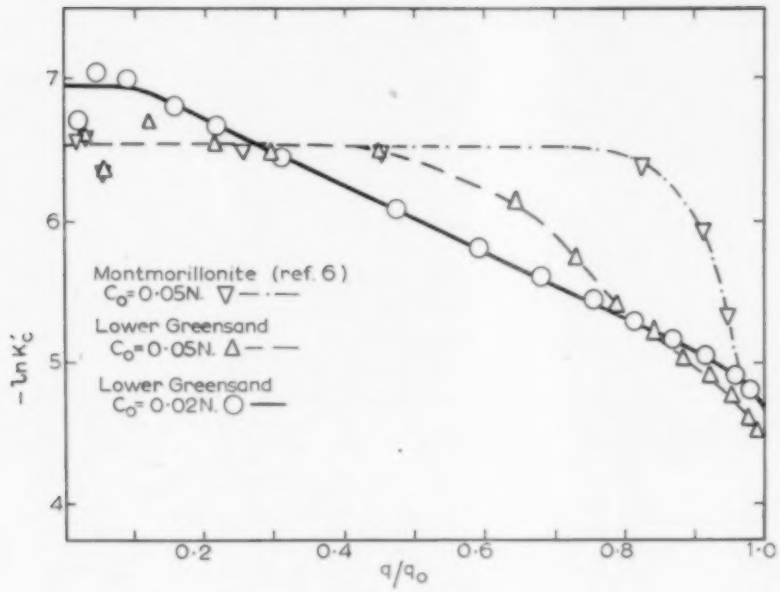

FIG. 6.—Variation of $\ln K_c'$ with q/q_0.

TABLE 2.—THERMODYNAMIC EQUILIBRIUM CONSTANTS FOR THE EXCHANGE $2CsX + Sr^{2+} \rightleftharpoons 2Cs^+ + SrX_2$.

Exchanger	C_0, equivts./l	$\ln K$	$10^4 K$
Lower Greensand soil	0·02	—6·96	$9·5_2$
Lower Greensand soil	0·05	—7·00	$9·1_3$
Montmorillonite[6]	0·05	—7·32	$6·6_3$

q/q_0 at a point Q on the isotherm the solid-phase activity coefficients in the present system are given by the expressions

$$\ln f_{Sr}(Q) = \ln f_{Sr}(A) - \left(\frac{q}{q_0}\right)_Q - \left(\frac{q}{q_0}\right) . \ln K_c(Q) + \int_0^Q \ln K_c . d\left(\frac{q}{q_0}\right) - 2\int_A^Q N_s . d \ln a_s, \tag{7}$$

$$\ln f_{Cs}^2(Q) = \ln f_{Cs}^2(B) + \left(1 - \frac{q}{q_0}\right)_Q + \left(1 - \frac{q}{q_0}\right)_Q . \ln K_c(Q) - \int_Q^1 \ln K_c . d\left(\frac{q}{q_0}\right) + 2\int_Q^B N_s . d \ln a_s. \tag{8}$$

By introducing the same simplifying assumptions as before, we obtain values of f_{Sr} and f_{Cs} as functions of q/q_0, where q again refers to Cs uptake; these are plotted in Fig. 7, together with the values for montmorillonite. It will be seen that in general the behaviour of Cs is not far from ideal over the whole range, but that Sr becomes

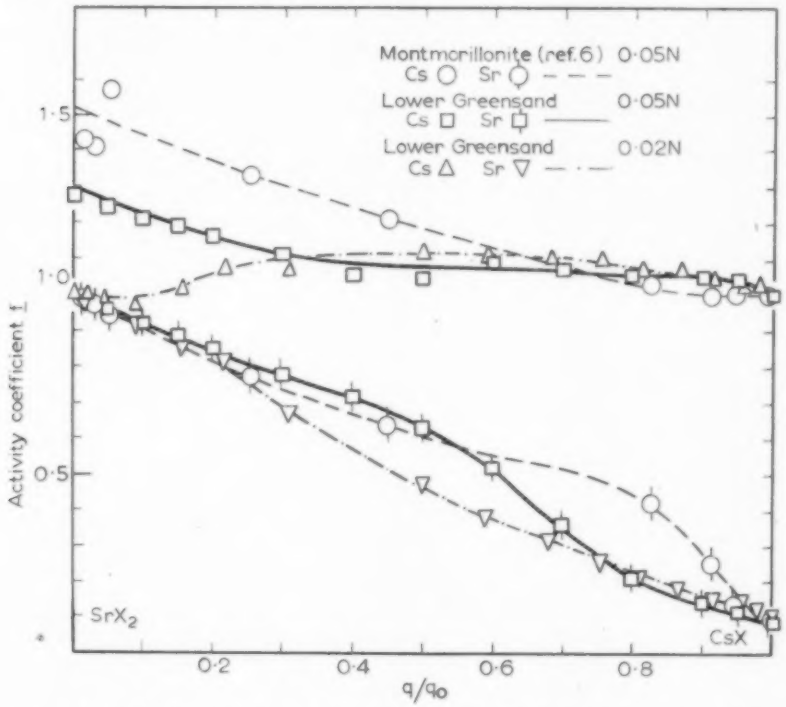

FIG. 7.—Solid-phase activity coefficients in mixed soils. Standard state: pure mono-ion soil in contact with solution of corresponding ion at infinite dilution.

progressively less ideal as its concentration in the clay increases. It is difficult to estimate the degree of ideality with certainty, since the derivation is based on f_{Sr} and f_{Cs} being unity in the pure clays in contact with solutions not at infinite dilution.

Acknowledgements—We are indebted to Mr. G. BROWN, of Rothamsted Experimental Station, for X-ray examination of clay fractions of the soil, and to Professor HENRY C. THOMAS, of Yale University, for permission to quote from work in course of publication.

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Spontaneous Fission Half-life of Cm^{246}*

(*Received* 27 *January* 1956)

THE mole percentages of Cm^{246} in the curium samples produced to date by multiple neutron capture in Pu^{239} are less than 2%.[1, 2] Samples containing such low isotopic abundances of Cm^{246} are undesirable for the spontaneous fission half-life determination of Cm^{246}, since it is expected that this value will be of the same magnitude as the spontaneous fission half-life of Cm^{244}. In addition, longer neutron irradiations of Cm^{244} will not be very helpful in that higher-mass isotopes, e.g. Cm^{247} and Cm^{248}, of curium are formed, and existing spontaneous fission systematics[3] predict a sizable spontaneous fission contribution from the higher even A isotopes due to their shorter spontaneous fission half-lives.

In a recent communication,[4] the production of Pu^{246} from uranium which had been subjected to a very high instantaneous neutron flux in a thermonuclear explosion was mentioned. The source of our curium sample used for the measurement of the spontaneous fission half-life of Cm^{246} was a plutonium fraction which had been chemically separated from the uranium and transplutonium elements one week after a thermonuclear explosion. This delay in the chemical separation of the plutonium allowed time for the Pu^{248} and Pu^{250} to decay substantially before the plutonium fraction was isolated. Neither of these isotopes has been discovered, but systematics indicate that a week is a sufficient period of time for Pu^{248} and Pu^{250} to decay through several half-lives.

The chemically separated plutonium fraction containing $4{\cdot}7 \pm 0{\cdot}8 \times 10^{-12}$ g of Pu^{246} was left undisturbed for sixteen days (half-lives[5] of Pu^{246} and Am^{246} are 11·2 days and 25 min, respectively), after which time a chemical separation of the curium was made. Am^{241}, present due to the beta decay of the Pu^{241} in the plutonium sample, served as a chemical tracer in that the chemistry used to separate the curium fraction did not discriminate against americium. The chemical yield of the Cm^{246} transferred to the counting plate, determined by alpha-counting the Am^{241}, was 86%. From the known limit on the spontaneous fission half-life[6] of Am^{241}, its calculated contribution to the spontaneous fission activity of the above sample is negligible (orders of magnitude less than the counter background).

The weight of Cm^{246} on the counting plate, $2{\cdot}6 \pm 0{\cdot}5 \times 10^{-12}$ g, was calculated from the known initial amount of Pu^{246} in the plutonium sample which had decayed for 16 days in conjunction with the chemical yield of the curium separation discussed above. The Pu^{246} isotopic content was measured in a 12-in., 60° mass spectrometer with a multiple-filament surface ionization source. This measurement and an alpha-activity determination (the specific alpha activity of our sample was calculated from the known plutonium alpha half-lives and the mass spectrometer data) were sufficient to calculate the weight of Pu^{246}.

The Cm^{246} plate was counted for 112 days, during which time 112 spontaneous fissions were recorded, giving 1·0 f/day. Backgrounds were run periodically during the above counting period, giving a result of 0·4 f/day. These results indicate that Cm^{246} is responsible for $(9{\cdot}6 \pm 4) \times 10^9$ spontaneous fissions/gram-hour, giving it a spontaneous fission half-life of $(2{\cdot}0 \pm 0{\cdot}8) \times 10^7$ years.

*Based on work performed under the auspices of the U.S. Atomic Energy Commission.

(1) STEVENS, STUDIER, FIELDS, MECH, SELLERS, FRIEDMAN, DIAMOND, and HUIZENGA, *Phys. Rev.* **94**, 974 (1954)
(2) W. C. BENTLEY *et. al.*, Geneva Conference on Peaceful Uses of Atomic Energy, Paper No. 809 (1955).
(3) J. R. HUIZENGA, *Phys. Rev.* **94**, 158 (1954).
(4) GHIORSO, THOMPSON, HIGGINS, SEABORG, STUDIER, FIELDS, FRIED, DIAMOND, MECH, PYLE, HUIZENGA, HIRSCH, MANNING, BROWNE, SMITH, and SPENCE, *Phys Rev.* **99**, 1048 (1955).
(5) ENGELKEMEIR, FIELDS, FRIED, PYLE, STEVENS, ASPREY, BROWNE, SMITH, and SPENCE, *J. Inorg. Nucl. Chem.* **1**, 345 (1955).
(6) HUIZENGA, MANNING, and SEABORG, Chap. 20, *The Actinide Elements*, (NNES, Div. IV, Vol. 14A McGraw-Hill Book Co., New York, 1954).

This value is comparable to the $1{\cdot}4 \times 10^7$ year spontaneous fission half-life of Cm^{244} in agreement with expectations. The alpha particles of Cm^{246} (the intensity calculated with the aid of the measured alpha half-life[1] is approximately 1 count/minute) were not directly observed by alpha-pulse analysis, due to the much larger Am^{241} activity, which is composed of several alpha energy groups, the lowest energy group being very close in energy to that of the main Cm^{246} alpha group.

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The Nature of the Silicon-oxygen Bond

(*Received* 30 *January* 1956)

On account of the industrially important silicones and the petrologically important silicates, the silicon-oxygen bond occupies a special position in chemistry. The high degree of polarity of this bond has long been recognized, but it is now fairly certain that $d\pi$—$p\pi$ bonding, involving the p electrons of oxygen and the vacant $3d$ electron orbitals of silicon, also contributes to the bond system. The extent of $d\pi$—$p\pi$ bonding in a given situation naturally depends on the groups attached to silicon and oxygen, but some multiple bonding occurs even when electron-releasing methyl groups are attached to silicon, as in trimethylsilanol, $(CH_3)_3SiOH$. In this laboratory we are examining the nuclear magnetic resonance absorption spectra of a number of silicon compounds. Thus we have compared the chemical shift of the hydroxyl proton in trimethylsilanol with that of the hydroxyl proton in trimethylcarbinol. On the basis of the older concepts of electronegativity, silicon should be less electron-attracting than carbon, so the proton bound to oxygen in $(CH_3)_3SiOH$ should be relatively more screened than the proton bound to oxygen in $(CH_3)_3COH$. However, appreciable silicon-oxygen $d\pi$—$p\pi$ bonding would lead to the reverse effect.

We have found that the hydroxyl proton in trimethylsilanol is screened only to about the same extent as the hydroxyl proton in propyl alcohol and is less screened than the corresponding proton in trimethylcarbinol. This observation supplies good qualitative evidence for $d\pi$—$p\pi$ bonding in $(CH_3)_3SiOH$, assuming effects due to molecular association are similar or negligible in both trimethylcarbinol and silanol. It is interesting to note that, whereas both propanol and trimethylsilanol[1] form sodium derivatives, trimethylcarbinol does not do so. This chemical observation supports our nuclear magnetic resonance evidence for the relatively more protonic character of the hydrogen bonded to oxygen in $(CH_3)_3SiOH$ compared with that bonded to oxygen in $(CH_3)_3COH$.

Because of the electron-releasing properties of methyl groups, the back co-ordination from oxygen to silicon in trimethylsilanol would be less than that in disiloxane. The chemical bonding in disiloxane and a number of other silicon compounds was discussed by us in the first issue of this journal,[2] where it was pointed out that $d\pi$—$p\pi$ bonding in $(SiH_3)_2O$ might result in the silicon-oxygen-silicon bond angle being very large, even perhaps 180°. It is, therefore, interesting that a careful study[3] of the infra-red and Raman spectra of disiloxane supports this suggestion.

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* Natvar Fellow, Harvard University, 1954–56.

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